



Europäisches Patentamt

(19) European Patent Office

Office européen des brevets

(11) Publication number:

**O 043 562**

B1

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **13.06.84**

(51) Int. Cl.: **C 01 B 25/36,**

(21) Application number: **81105146.5**

B 01 J 27/16, B 01 J 29/04

(22) Date of filing: **02.07.81**

---

(54) Crystalline metallophosphate compositions.

(30) Priority: **07.07.80 US 166333**

(73) Proprietor: UNION CARBIDE CORPORATION  
Old Ridgebury Road  
Danbury Connecticut 06817 (US)

(43) Date of publication of application:  
**13.01.82 Bulletin 82/2**

(72) Inventor: Wilson, Stephen Thomas  
1024 East Main Street  
Shrub Oak, N.Y. (US)  
Inventor: Lok, Brent Meitak  
17A Deerwood Drive  
New City (10956) (US)  
Inventor: Flanigan, Edith Marie  
502 Woodland Hills Road  
White Plains, N.Y. (US)

(46) Publication of the grant of the patent:  
**13.06.84 Bulletin 84/24**

(84) Designated Contracting States:  
**AT BE CH DE FR GB IT LI NL SE**

(56) References cited:  
EP - A - 0 022 620  
DE - A - 2 403 707  
DE - A - 2 542 230  
DE - A - 2 730 228  
US - A - 3 227 519  
US - A - 3 386 801  
US - A - 3 947 482

(74) Representative: Eggert, Hans-Gunther, Dr.  
Räderscheidtstrasse 1  
D-5000 Köln 41 (DE)

**EP O 043 562 B1**

CHEMICAL SOCIETY REVIEWS, Vol. 6, 1977,  
London J.H. MORRIS et al. "The Chemistry and  
Binding Properties of Aluminium Phosphates"  
pages 173 to 194

---

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

**Description**

The present invention relates in general to a novel family of crystalline compositions and to the method for their synthesis. More particularly it relates to crystalline microporous aluminophosphate compositions and to hydrothermal processes for preparing same.

Molecular sieves of the crystalline zeolite type are well known in the art and now comprise over 150 species of both naturally occurring and synthetic compositions. In general the crystalline zeolites are aluminosilicates whose frameworks are formed from  $\text{AlO}_4^-$  and  $\text{SiO}_4$  tetrahedra joined by the sharing of oxygen atoms and characterized by having pore openings of uniform dimensions, having a significant ion-exchange capacity and being capable of reversibly desorbing an adsorbed phase which is dispersed through the internal voids of the crystal without displacing any atoms which make up the permanent crystal structure.

Other crystalline microporous phases which are not zeolitic, i.e. do not contain  $\text{AlO}_4^-$ -tetrahedra as essential framework constituents, but which exhibit the ion exchange and/or adsorption characteristics of the zeolitic phases are also known. Metallorganosilicates which are said to possess ion-exchange properties, have uniform pores and are capable of reversibly adsorbing molecules having molecular diameters of about 0.6 nm or less are reported in U.S.—A—3,941,871 issued March 2, 1976 to Dwyer et al. Also a pure silica polymorph having molecular sieving properties and a neutral framework containing no cations or cation sites is defined in U.S.—A—4,061,724 issued December 6, 1977 to R. W. Gross et al.

We have now discovered a new class of molecular sieve materials which are microporous three-dimensional crystalline aluminophosphate phases having uniform pore dimensions ranging from 0.3 to 1.0 nm and capable of making size selective separations of molecular species.

The chemistry of aluminum phosphates has been reviewed by J. H. Morris et al. (Chem. Soc. Rev., 6, 173 (1977)). The phosphates with an  $\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5$  molar ratio of 1:1 are the most common, and have been the most widely studied. Anhydrous  $\text{AlPO}_4$  is isoelectronic and isostructural with silica and exists in quartz (as berlinitite), tridymite, and cristobalite forms possessing frameworks of alternating  $\text{AlO}_4^-$  and  $\text{PO}_4$  tetrahedra. In addition to these, F. D'Yvoire [Bull. Soc. Chim. France, 1762 (1961)] has described five anhydrous crystalline  $\text{AlPO}_4$  forms which have no silica analogs.

Two hydrates of  $\text{AlPO}_4$  with the stoichiometry  $\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$ , metavariscite and variscite, occur in natural and synthetic forms. Their structures were determined by Kniep and coworkers (Acta Cryst., B29, 2292 (1973); ibid., B33 263 (1977)), and both can be described as frameworks of alternating octahedral  $\text{AlO}_4(\text{H}_2\text{O})_2$  and tetrahedral  $\text{PO}_4$  units. In both the metavariscite and variscite structures the  $\text{H}_2\text{O}$  is chemically bound to the Al and, although small amounts of this water can be removed reversibly, complete dehydration is irreversible and leads to significant structural changes and the formation of anhydrous  $\text{AlPO}_4$  phases.

In addition to these, six crystallographically unique, metastable hydrates have been synthesized by F. D'Yvoire (ibid.). Of these, four are reported to be reversibly dehydrated under mild conditions to yield anhydrous phases, but in each case significant changes in framework topology occurred. These changes were reported to be reversible by rehydration. It is possible therefore that the interaction between water and these aluminophosphate phases results in chemical bonding, such as the formation of  $\text{AlO}_4(\text{H}_2\text{O})_2$  octahedra, rather than physisorption.

The hydrothermal synthesis of aluminophosphates in the presence of various alkali metal, alkaline earth, and  $\text{NH}_4^+$  cations has been reported by Haseman and coworkers (Soil Sci. Soc. Proceed., 45, 76 (1950); Soil Sci., 70, 257—271 (1950)), by Cole and Jackson (J. Phys. Chem.), 54, 128—142 (1950)), and by Golub and Boldog (Russ. Jour., Inorg., Chem., 21, 45 (1976)). A variety of known minerals (e.g. palmierite, taranakite, wavellite, variscite) and many novel crystalline materials were obtained. Virtually all of these materials had Al/P ratios different from 1.0. Although most of the products had appreciable  $\text{H}_2\text{O}$  content only one product was examined by X-ray powder diffraction after dehydration. This product, taranakite, became amorphous at 125°C. The stability of the other phases is unknown.

R. M. Barrer and D. J. Marshall (J. Chem. Soc., 6616 (1965)) attempted to substitute P for Si during hydrothermal crystallization of mixed frameworks analogous to aluminosilicates. The crystalline products obtained from synthesis mixtures containing sources of Al, Si, and P were predominately aluminosilicates (e.g. montmorillonite, analcite, and cancrinite) and phosphates (e.g. hydroxyapatite). Several unidentified crystalline solids were observed, characterized solely by their X-ray powder diffraction patterns. Evidence for phosphorus incorporation in the aluminosilicate structures or silicon incorporation in the hydroxyapatites was not obtained, however.

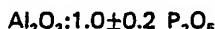
G. Kuehl has used phosphate as a complexing ion for aluminum in the hydrothermal synthesis of certain zeolites (Proceedings of the London Conf. on Molecular Sieves, April 1967, p. 85; Inorg. Chem., 10, 2488 (1971)). Presumably the pH sphaite complex is some of the aluminum, lowering the effective concentration of the more reactive hydrox aluminate species in the reaction mixture and, thereby, increases the ratio of silicate to hydrox aluminate. The zeolite products had a higher Si/Al ratio than normal and presumably no incorporation of P into the zeolite frameworks was observed. In one case, a high-silica form of zeolite A contained phosphate intercalated in the sodalite cages.

## O 043 562

In an attempt to isolate the aluminophosphate species formed when phosphate is added to a zeolite synthesis mixture, G. Kuehl prepared the crystalline compounds  $[(\text{CH}_3)_4\text{N}]_3[\text{Al}(\text{PO}_4)_2] \cdot X \text{ H}_2\text{O}$  where  $X=10, 4$ , and  $1.5$ . They were characterized by X-ray powder diffraction, thermal, and elemental analysis, and were described as salts containing isolated  $\text{Al}(\text{PO}_4)_2(\text{OH}_2)_x^{3-}$  units. Removal of all the  $\text{H}_2\text{O}$  caused the decomposition of these compounds (U.S. Patent No. 3,386,801 (1968); J. Inorg. Nucl. Chem., 31, 1943 (1969)).

The novel generic class of aluminophosphates of the present invention having an essential crystalline framework structure whose chemical composition expressed in terms of molar ratios of oxides is:

10



and is characterized in that said framework structure being microporous in which the pores are uniform and in each species have nominal diameters within the range of from  $0.3$  to  $1.0$  nm; an intracrystalline adsorption capacity for water at  $6.13$  mbar and  $24^\circ\text{C}$  of at least  $3.5$  weight percent, the adsorption of water being completely reversible while retaining the same essential framework topology in both the hydrated and dehydrated state. By the term "essential framework topology" is meant the spatial arrangement of the primary  $\text{Al}-\text{O}$  and  $\text{P}-\text{O}$  bond linkages. No change in the framework topology indicates that there is no disruption of these primary bond linkages.

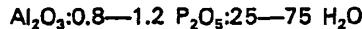
20 The present aluminophosphates are prepared by hydrothermal crystallization of a reaction mixture prepared by combining a reactive source of phosphate, alumina and water and at least one structure-directing or templating agent which can include an organic amine and a quaternary ammonium salt. In the as-synthesized form the structure-directing agent is contained within the framework structure of the aluminophosphate in amounts which vary from species to species but usually does not exceed one mole per mole of  $\text{Al}_2\text{O}_3$  thereof. This structure-directing agent is readily removed by water washing or calcination and does not appear to be an essential constituent of the product aluminophosphate as evidenced by essentially complete absence of ion-exchangeability of as-synthesized compositions and also the absence of any internally-contained organic molecules in the as-synthesized form of at least one species of the generic class. Evidence that a structure-directing agent is a critical constituent is contained in certain of the illustrative examples appearing hereinafter, wherein reaction mixtures otherwise identical to those which yield products of the present invention except for the presence of templating agents, yield instead the previously known aluminophosphate phases  $\text{AlPO}_4 \cdot 1.1-1.3 \text{ H}_2\text{O}$ ,  $\text{AlPO}_4$ -tridymite,  $\text{AlPO}_4$ -quartz and  $\text{AlPO}_4$ -cristobalite:

30 Broadly the preparative process comprises forming a reaction mixture which in terms of molar ratios of oxides is



40 and containing from about  $0.2$  to  $2.0$  moles of templating agent per mole of  $\text{Al}_2\text{O}_3$ . The reaction mixture is placed in a reaction vessel inert toward the reaction system and heated under autogeneous pressure at a temperature of at least about  $100^\circ\text{C}$ , preferably between  $100^\circ\text{C}$  and  $300^\circ\text{C}$ , until crystallized, usually a period from  $2$  hours to  $2$  weeks. The solid crystalline reaction product is then recovered by any convenient method, such as filtration or centrifugation, washed with water and dried at a temperature between ambient and  $110^\circ\text{C}$  in air.

45 In a preferred crystallization method the source of phosphate is phosphoric acid, and source of alumina is a pseudo-boehmite hydrated aluminum oxide, the temperature is  $125^\circ\text{C}$  to  $200^\circ\text{C}$ , and the crystallization time is from one to seven days. The preferred ratio of oxides in the reaction mixture is



50

In general the most preferred reaction mixture contains per mole of  $\text{Al}_2\text{O}_3$  from about  $0.5-1.5$  moles of templating agent, from  $40-50$  moles of water and about  $1.0$  mole of  $\text{P}_2\text{O}_5$ .

55 Not all templating agents suitably employed in the preparation of certain species of aluminophosphates of this invention are suitable for the preparation of all members of the generic class. The relationship of specific templating agents to the individual product species is apparent from the illustrative Examples set forth hereinafter.

The method of preparation and the physical and chemical properties of the various members of the present class of novel aluminophosphates are illustrated and characterized, respectively, in the following examples. The species compounds are denominated as  $\text{AlPO}_4-n$  wherein "n" is a number specific to each individual member:

### Example 1

#### Preparation of $\text{AlPO}_4-5$

A reaction mixture was prepared by combining  $46.1$  grams of  $85\%$  orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and  $100.0$  grams of water, to which was added  $27.5$  grams of a hydrated aluminum oxide (a pseudo-

## 0 043 562

boehmite phase, 74.2 wt. %  $\text{Al}_2\text{O}_3$ , 25.8 wt. %  $\text{H}_2\text{O}$ , a commercial product available under the trademark Catapal SB of the Conoco Chemicals Division of Continental Oil Company, USA) and stirred until homogeneous. To this mixture was added 176.8 grams of an aqueous solution of 23 wt. % tetrapropylammonium hydroxide (TPAOH), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 150°C at autogenous pressure for 43 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at room temperature. The major phase in the product had an X-ray powder diffraction pattern characterized by the following data wherein "I" is the intensity and "d" the interplanar spacing. The product also contained a minor amount of another crystalline impurity.

15

	$2\theta$	d	$100 \times I/I_0$
20	7.50	11.8	100
	12.95	6.84	11
	14.95	5.93	28
	19.75	4.50	66
	20.95	4.24	63
	22.4	3.97	94
25	24.65	3.61	5
	26.00	3.43	37
	28.95	3.08	21
	30.05	2.97	22
	33.50	2.67	5
	34.50	2.60	19
30	36.95	2.43	5
	37.50	2.40	13
	40.75	2.21	1
	41.60	2.17	4
	42.45	2.13	4
	43.65	2.07	3
35	44.95	2.02	2
	47.70	1.91	6

This X-ray pattern and all other X-ray patterns appearing hereinafter were obtained using standard X-ray powder diffraction techniques. The radiation source was a high-intensity, copper target, X-ray tube operated at 50 kV and 40 mA. The diffraction pattern from the copper  $K\alpha$  radiation and graphite monochromator is suitably recorded by an X-ray spectrometer scintillation counter, pulse height analyzer and strip chart recorder. Flat compressed powder samples are scanned at  $2^\circ$  (2 theta) per minute, using a two second time constant. Interplanar spacings (d) are obtained from the position of the diffraction peaks expressed as  $2\theta$  where  $\theta$  is the Bragg angle as observed on the strip chart. Intensities are determined from the heights of diffraction peaks after subtracting background.

### Example 2

#### Preparation of $\text{AlPO}_4 \cdot 5$

50 (a) A reaction mixture was prepared by combining 23.1 grams of 85% orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and 44.0 grams of water, to which was added 13.7 grams of the same hydrated aluminum oxide employed in Example 1, and stirred until homogeneous. To this mixture was added 35.1 grams of an aqueous solution of 58 wt. % tetrapropylammonium hydroxide (TPAOH), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:

55



The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 150°C at autogenous pressure for 65 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at room temperature. A portion of the solids was submitted for X-ray analysis and chemical analysis.

Chemical analysis showed 7.5 wt. % C, 0.67 wt. % N, 34.2 wt. %  $\text{Al}_2\text{O}_3$ , 46.5 wt. %  $\text{P}_2\text{O}_5$ , 17.7 wt. % LOI (Loss on Ignition at 1000°C for 4 hr.) giving a product composition in molar oxide ratios of:

65



## O 043 562

The above product had an X-ray powder diffraction pattern essentially identical to that of the major phase in Example 1, and contained no crystalline impurities. This product was designated AlPO<sub>4</sub>-5.

(b) A portion of the solid crystalline product obtained from a similar procedure as in part (a) above and exhibiting an X-ray powder diffraction pattern essentially identical to that in Example 1 was calcined in air at about 500°C for 2 hours. The calcined product had an X-ray powder diffraction pattern essentially identical to that in Example 1.

### Example 3

#### Preparation of AlPO<sub>4</sub>-5

(a) A reaction mixture was prepared by combining 46.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 118.6 grams of water, to which was added 27.5 grams of a pseudo-boehmite phase (74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 29.2 grams of tripropylamine (Pr<sub>3</sub>N) and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 150°C at autogenous pressure for 70 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at room temperature. Chemical analysis showed 5.7 wt. % C, 0.72 wt. % N, 34.0 wt. % Al<sub>2</sub>O<sub>3</sub>, 48.1 wt. % P<sub>2</sub>O<sub>5</sub>, 16.4 wt. % LOI, giving a product composition in molar oxide ratios of:



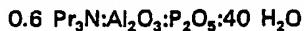
The above product had an X-ray powder diffraction pattern virtually identical to that of the major phase set forth in Example 1 and contained no crystalline impurities.

(b) A portion of the solid crystalline product obtained above was calcined in air at about 600°C for 2 hours. The calcined product had an X-ray powder diffraction pattern essentially the same as that of the as-synthesized product of part (a) above.

### Example 4

#### Preparation of AlPO<sub>4</sub>-5

35                    A reaction mixture was prepared by combining 23.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 59.6 grams of water, to which was added 13.7 grams of a hydrated aluminum oxide, (74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 8.6 grams of tripropylamine (Pr<sub>3</sub>N) and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:

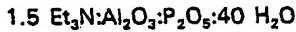


The reaction mixture was sealed in a stainless steel pressure vessel lined with an inert plastic material and heated in an oven at 150°C at autogenous pressure for 4 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at room temperature. The X-ray powder diffraction pattern of this product showed the crystalline AlPO<sub>4</sub>-5 product of example 3 as the major phase, with a minor amount of a crystalline impurity being also present.

### Example 5

#### Preparation of AlPO<sub>4</sub>-5

50                    A reaction mixture was prepared by combining 46.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 119.2 grams of water, to which was added 27.5 grams of a hydrated aluminum oxide (74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 30.4 grams of triethylamine (Et<sub>3</sub>N), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



60                    The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 200°C at autogenous pressure for 27 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at room temperature. Chemical analysis of the product indicated the presence of 4.8 wt. % C, 0.97 wt. % N, 35.3 wt. % Al<sub>2</sub>O<sub>3</sub>, 49.7 wt. % P<sub>2</sub>O<sub>5</sub> and 13.6 wt. % LOI, giving a product composition in molar oxide ratios of:



## O 043 562

The above product had an X-ray powder diffraction pattern essentially identical to that of the AlPO<sub>4</sub>-5 product of example 1 and contained no crystalline impurities.

### Example 6

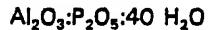
#### 5 Preparation of AlPO<sub>4</sub>-5

(a) A reaction mixture was prepared by combining 18.5 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 45.9 grams of water, to which was added 13.7 grams of a pseudo-boehmite phase (74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 25.9 grams of an aqueous solution of 57 wt. % tetrapropylammonium hydroxide (TPAOH), and the mixture in molar oxide ratios was:



The reaction mixture was placed in a stainless steel pressure vessel lined with an inert plastic material and heated in an oven at 150°C at autogenous pressure for 72 hours. The solid reaction product was recovered by repeated centrifugation and washing with water, followed by filtration, washing, and drying in air at room temperature. The X-ray powder diffraction pattern of the dried product showed the major phase to be identical to AlPO<sub>4</sub>-5 of example 1.

(b) A reaction mixture free of a structure-directing agent was prepared by combining 46.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 120 grams of water, to which was added 27.5 grams of the same hydrated aluminum oxide as in part (a) above, and stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:

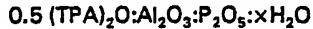


25 The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 150°C at autogenous pressure for 72 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. The resulting product had an X-ray powder diffraction pattern indicating a mixture of known AlPO<sub>4</sub> phases:  
30 AlPO<sub>4</sub> 1.1—1.3 H<sub>2</sub>O, and two structural analogs of crystalline silica, namely AlPO<sub>4</sub> (quartz) and AlPO<sub>4</sub> (tridymite). An identical reaction mixture heated at 200° for 24 hours produced a mixture of the same known AlPO<sub>4</sub> phases, the major products being AlPO<sub>4</sub> (quartz) and AlPO<sub>4</sub> (tridymite). No microporous AlPO<sub>4</sub> phases of the present invention were observed.

#### 35 Example 7

#### Preparation of AlPO<sub>4</sub>-5

A reaction mixture was prepared by combining 37.8 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 177 grams of water, to which was added 67 grams of aluminum isopropoxide and stirred until homogeneous. The mixture was filtered and washed with water. To this mixture was added 145 grams of an aqueous solution of 23 wt. % tetrapropylammonium hydroxide (TPAOH), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



45 The reaction mixture was placed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 150°C at autogenous pressure for 276 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. The dried product was AlPO<sub>4</sub>-5 as indicated by an X-ray powder diffraction pattern which was essentially the same as the AlPO<sub>4</sub>-5 in example 1.

#### 50 Examples 8—26

#### Preparation of AlPO<sub>4</sub>-5

A procedure similar to that in example 3 was followed except where indicated in Table A below. The composition of each final mixture in molar oxide ratios was:



except where noted in Table A. A portion of the solid product from each reaction was examined by X-ray analysis and in each case a phase characterized by an X-ray powder diffraction pattern essentially the same as the AlPO<sub>4</sub>-5 phase in example 1 was observed alone or in admixture with other products.

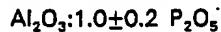
## O 043 562

TABLE A

Example #	R	Reaction time (hrs.)	Reaction temp. (°C)
5	8 $(C_2H_5)_4NOH$ (tetraethylammonium hydroxide)	24	200
	9 $N(CH_2CH_2OH)_3$ (triethanolamine)	72	150
	10 piperidine	24	150
	11 2-methylpyridine	168	150
	12 cyclohexylamine	168	150
10	13 N,N-dimethylbenzylamine	168	150
	14 N,N-diethylethanolamine	24	200
	15 dicyclohexylamine	24	150
	16 N,N-dimethylethanolamine	24	150
	17 $[(CH_3)_3NCH_2CH_2OH)OH^1$	52	150
15	18 N,N-dimethylpiperazine <sup>1</sup>	24	200
	19 1,4-diazabicyclo(2.2.2)octane DABCO <sup>2</sup>	192	200
	20 N-methyl-diethanolamine <sup>1</sup>	24	200
	21 N-methyl-ethanolamine <sup>1</sup>	24	200
	22 N-methylpiperidine	24	200
20	23 3-methylpiperidine	168	150
	24 N-methylcyclohexylamine	24	200
	25 3-methylpyridine	24	150
	26 4-methylpyridine	168	150

<sup>25</sup> <sup>1</sup>The final reaction mixture contains 50 H<sub>2</sub>O.<sup>2</sup>The final reaction mixture contains 0.5 DABCO.

The species AlPO<sub>4</sub>-5 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 2, below:

35	2θ	d	100×l <sub>1</sub> /l <sub>0</sub>
	7.4—7.6	11.9—11.6	100
	14.8—15.3	5.97—5.83	13—43
40	19.7—20.1	4.51—4.42	39—92
	20.8—21.2	4.27—4.19	37—87
	22.3—22.7	3.99—3.93	62—118
	25.9—26.3	3.44—3.39	22—35

All of the AlPO<sub>4</sub>-5 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 3, below:

50	2θ	d	100×l <sub>1</sub> /l <sub>0</sub>
	7.4 — 7.6	11.9 — 11.6	100
	12.9 — 13.15	6.86 — 6.73	9—12
	14.85—15.2	5.97—5.83	13—43
	19.7 — 20.1	4.51—4.42	39—92
55	20.8 — 21.2	4.27—4.19	37—87
	22.3 — 22.7	3.99—3.92	62—118
	24.55—24.9	3.63—3.58	4—8
	25.9 — 26.25	3.44—3.39	22—32
	28.9 — 29.2	3.09—3.06	11—18
60	30.0 — 30.4	2.98—2.94	12—23
	33.5 — 33.85	2.67—2.65	4—9
	34.5 — 35.1	2.60—2.56	11—17
	36.9 — 37.2	2.44—2.42	3—5
	37.5 — 37.8	2.40—2.38	7—16
65	40.8 — 40.85	2.21—2.21	0—1
	41.5 — 42.0	2.18—2.15	2—3

## O 043 562

TABLE 3 (c ntd.)

	2θ	d	100×I/I <sub>0</sub>
5	42.25—42.5	2.14—2.13	0—4
	42.7—42.8	2.12—2.11	0—3
	43.6—44.0	2.08—2.06	0—2
	45.0—45.4	2.01—2.00	0—2
	46.2	1.96	0—1
	47.8	1.90	0—4
10	48.0—48.4	1.90—1.87	0—5
	51.5—51.6	1.77—1.77	0—2
	52.0	1.76	0—2
	55.8—56.0	1.65—1.64	0—2

## Example 27

15 Preparation of AlPO<sub>4</sub>-8

(a) A reaction mixture was prepared by combining 8.9 grams of 85% orthophosphoric acid ( $H_3PO_4$ ) and 6 grams of water, to which was added 5.3 grams of a hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt. %  $Al_2O_3$ , 25.8 wt. %  $H_2O$ ), and 6.0 grams of water, and stirred until homogeneous. To this mixture was added 27.2 grams of an aqueous solution of 37 wt. % tetrabutylammonium hydroxide (TBAOH), and 2.0 grams of water and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratio was:



25 The reaction mixture was sealed in a stainless steel pressure vessel lined with an inert plastic material and heated in an oven at 150°C at autogenous pressure for 145 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 115°C. Chemical analysis showed the product to contain 0.2 wt. % C, <0.05 wt. % N, 34.7 wt. %  $Al_2O_3$ , 46.6 wt. %  $P_2O_5$ , 18.4 wt. % LOI, giving a product composition in molar oxide ratios of:



The major phase in the above product had an X-ray powder diffraction pattern characterized by the following data wherein "I" is the intensity and "d" the interplanar spacing; the product also contained a minor amount of a crystalline impurity.

	2θ	d	100×I/I <sub>0</sub>
40	5.3	16.7	80
	6.5	13.6	100
	10.0	8.84	17
	10.8	8.19	2
	14.6	6.07	4
	16.1	5.56	16
45	18.8	4.72	2
	19.8	4.48	8
	20.2	4.40	12
	21.25	4.19	82
	21.9	4.06	18
50	22.4	3.97	39
	22.7	3.92	(sh)*
	23.55	3.77	3
	24.15	3.68	11
	24.9	3.58	11
55	27.1	3.29	2
	28.2	3.16	5
	31.35	2.853	4
	32.9	2.722	3
	34.2	2.622	1
60	35.6	2.522	3
	38.0	2.368	9
	38.4	2.344	3 (sh)*
	43.2	2.094	2
	46.9	1.937	1
	49.5	1.841	3

65 \*sh=shoulder

## O 043 562

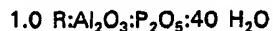
This product was designated AlPO<sub>4</sub>-8. It is to be noted that only trace amounts of the tetrabutylammonium templating compound were present in the reaction product solids. This may indicate that a templating mechanism different from that in most other species of this invention is involved.

5 (b) A portion of the solid crystalline product obtained above was calcined in air at about 600°C for 2 hours. The calcined product had an X-ray powder diffraction pattern essentially the same as that of the product of part (a) above.

### Examples 28—30

#### 10 Preparation of AlPO<sub>4</sub>-8

A procedure similar to that in example 27 was followed except where indicated in Table B. The composition of each final reaction mixture in molar oxide ratios was:



15

where R is indicated in Table B. In each case a product phase characterized by an X-ray powder diffraction pattern essentially the same as that in example 27 was observed. Some extraneous phases were also present.

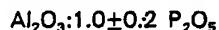
20

TABLE B.

	Example #	Organic used (R)	Digestion time (hrs.)	Temp (°C)
25	28	(n-C <sub>5</sub> H <sub>11</sub> ) <sub>4</sub> NOH	24	150
	29	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NH	72	150
	30	(n-C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> NH*	24	150

\* Small amount of acetone used to wash solid product.

30 The species AlPO<sub>4</sub>-8 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



35 and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 4 below:

TABLE 4.

	2θ	d	100xI/I <sub>0</sub>
40	5.3—5.4	16.7—16.4	80—100
	6.5—6.65	13.6—13.3	30—100
	19.7—19.8	4.51—4.48	8—29
	21.2—21.3	4.19—4.17	46—82
	21.8—21.9	4.08—4.06	14—56
45	22.4—22.9	3.97—3.88	35—39

All of the AlPO<sub>4</sub>-8 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 5 below:

50

TABLE 5

	2θ	d	100xI/I <sub>0</sub>
55	5.3—5.4	16.7—17.4	80—100
	6.5—6.65	13.6—13.3	30—100
	9.9—10.1	8.9—8.8	15—20
	10.75—10.8	8.23—8.19	2—9
	14.6—14.8	6.07—5.99	4—17
	16.1—16.2	5.50—5.47	7—16
60	18.8—18.9	4.72—4.70	2—12
	19.7—19.8	4.51—4.48	8—29
	20.1—20.2	4.42—4.40	9—12
	21.2—21.3	4.19—4.17	46—82
	21.8—21.9	4.08—4.06	14—56
65	22.4—22.5	3.97—3.95	35—39
	22.7—22.9	3.92—3.88	

## O 043 562

TABLE 5 (contd.)

 $2\theta$ 

d

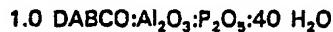
100*xI/I<sub>0</sub>*

5	23.55—23.65 24.1 —24.2 24.9 —25.1 27.1 —27.2 28.2 —28.3 31.35—31.4	3.77— 3.76 3.69— 3.68 3.58— 3.55 3.29— 3.28 3.16— 3.15 2.853—2.849	3—7 9—11 11—15 2—16 4—8 4—6
10	32.9 34.2 —34.3 35.6 38.0 —38.2 38.4 —38.6 43.2 —43.3	2.722 2.622—2.614 2.522 2.368—2.356 2.344—2.332 2.094—2.090	3—8 1—2 0—3 9—16 3—18 2—4
15	46.9 —47.0 49.4 —49.5	1.937—1.933 1.845—1.841	1—2 2—4

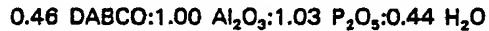
## Example 31

Preparation of AlPO<sub>4</sub>-9

(a) A reaction mixture was prepared by combining 27.6 grams of 85% orthophosphoric acid ( $H_3PO_4$ ) and 36.0 grams of water, to which was added 16.5 grams of a hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt. %  $Al_2O_3$ , 25.8 wt. %  $H_2O$ ), and stirred until homogeneous. To this mixture was added 13.5 grams of 1,4-diazabicyclo[2.2.2]octane (DABCO) dissolved in 24.0 grams of water, then 11.7 grams of water, and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was sealed in a stainless steel pressure vessel lined with inert plastic and heated in an oven at 200°C at autogenous pressure for 336 hours. The solid reaction product was recovered and washed by repeated centrifugation with water, and dried in air at 110°C. A portion of the solids was subjected to X-ray analysis and chemical analysis. Chemical analysis showed 10.6 wt. % C, 3.9 wt. % N, 32.5 wt. %  $Al_2O_3$ , 46.5 wt. %  $P_2O_5$ , 19.0 wt. % LOI, giving a product composition in molar oxide ratios of:



The above product, denominated AlPO<sub>4</sub>-9, had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

	$2\theta$	d	100 <i>xI/I<sub>0</sub></i>
45	8.4 11.1 12.5 14.0 15.1 16.8	10.5 7.97 7.08 6.33 5.87 5.28	12 43 18 6 5 11
50	18.3 19.3 21.0 21.9 22.3 22.8 25.4 25.7 26.5 27.7 28.5 30.6 31.45 31.8 32.4 33.15	4.85 4.60 4.23 4.06 3.99 3.90 3.51 3.47 3.36 3.22 3.13 2.92 2.843 2.814 2.763 2.702	29 11 100 30 18 30 38 79 13 21 29 5 10 27 <1 12
55			
60			
65			

**O 043 562**

	2θ	d	100×I/I <sub>0</sub>
5	33.7	2.660	18
	34.3	2.614	5
	34.8	2.578	3
	35.5	2.529	4
	36.4	2.468	1
	37.8	2.380	4
10	38.35	2.347	10
	38.45	2.341	(sh)*
	38.9	2.315	10
	41.3	2.186	2
	42.15	2.144	6
	42.6	2.122	4
15	44.55	2.034 }	3
	44.65	2.029 }	
	46.5	1.953	2
	48.0	1.895	3
	48.4	1.881	1
	49.75	1.833	7
20	50.2	1.817	9
	51.0	1.791	1
	51.7	1.768	(sh)* } 11
	51.9	1.762	11
	53.65	1.708 }	4
	53.8	1.704 }	
25	55.35	1.660	7

\*sh=shoulder

30 (b) The procedure and gel composition of part (a) above were repeated except that the reaction mixture was heated for 168 hours. AlPO<sub>4</sub>-9 was produced.

The species AlPO<sub>4</sub>-9 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is

35 Al<sub>2</sub>O<sub>3</sub>:1.0±0.2 P<sub>2</sub>O<sub>5</sub>

and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 6 below:

40	2θ	TABLE 6	
		d	100×I/I <sub>0</sub>
45	11.1 — 11.15	7.97—7.94	43—68
	12.5 — 12.65	7.08—7.00	12—100
	18.25—18.35	4.86—4.83	19—47
	21.0 — 21.1	4.23—4.21	41—100
	25.4 — 25.6	3.51—3.48	38—82
	25.7 — 25.8	3.47—3.45	0—79

50 All of the AlPO<sub>4</sub>-9 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 7 below:

55	2θ	TABLE 7	
		d	100×I/I <sub>0</sub>
60	8.4 — 8.5	10.5 — 10.4	<1—22
	10.8	8.19	(sh)
	11.1 — 11.15	7.97 — 7.94	43—68
	12.5 — 12.65	7.08 — 7.00	12—100
	14.0 — 14.2	6.33 — 6.24	2—8
	15.1 — 15.25	5.87 — 5.81	4—6
65	16.8 — 16.85	5.28 — 5.26	3—13
	18.25—18.35	4.86 — 4.83	19—47
	19.3 — 19.5	4.60 — 4.55	2—15
	21.0 — 21.1	4.23 — 4.21	41—100

## O 043 562

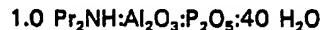
TABLE 7 (contd.)

	2θ	d	100×I/I <sub>0</sub>
5	21.9 — 22.05	4.06 — 4.03	11—39
	22.2 — 22.3	4.00 — 3.99	(sh)—20
	22.7 — 22.8	3.92 — 3.90	30—39
	25.4 — 25.6	3.51 — 3.48	38—82
	25.7 — 25.8	3.47 — 3.45	0—79
	26.5 — 26.7	3.36 — 3.34	13—16
10	27.7 — 27.9	3.22 — 3.20	4—21
	28.2	3.16	0—(sh)
	28.45—28.55	3.136—3.126	16—36
	30.3 — 30.7	2.950—2.912	5—21
	31.45—31.6	2.844—2.831	(sh)
	31.8 — 31.85	2.814—2.810	14—30
15	33.15—33.3	2.702—2.691	5—16
	33.6 — 33.7	2.667—2.660	12—18
	34.0	2.637	0—6
	34.3 — 34.5	2.614—2.600	5—6
	34.8 — 34.9	2.578—2.571	0—3
	35.5 — 35.7	2.529—2.515	4—6
20	36.1 — 36.4	2.488—2.468	1—3
	37.8 — 38.0	2.380—2.368	2—7
	38.35—38.5	2.347—2.338	4—10
	38.9 — 39.1	2.315—2.304	8—10
	41.1 — 41.3	2.196—2.186	0—2
	42.1 — 42.2	2.146—2.141	3—6
25	42.6 — 42.7	2.122—2.118	2—4
	44.55—44.85	2.034—2.021	1—3
	46.3 — 46.7	1.961—1.945	2—4
	48.0 — 48.05	1.895—1.893	3—4
	48.4 — 48.7	1.881—1.870	<1—3
	49.75—50.0	1.833—1.824	0—14
30	50.2 — 50.3	1.817—1.814	0—14
	51.0 — 51.1	1.791—1.787	<1—2
	51.7 — 51.8	1.768—1.765	(sh)—12
	51.9 — 52.1	1.762—1.755	7—11
	53.65—54.0	1.708—1.698	3—4
	55.3 — 55.5	1.661—1.656	6—8
40			

## Example 32

Preparation of AlPO<sub>4</sub>-11

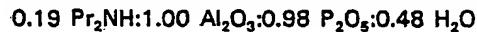
(a) A reaction mixture was prepared by combining 46.0 grams of 85% orthophosphoric acid ( $H_3PO_4$ ) and 119.2 grams of water, to which was added 27.5 grams of the same hydrated aluminum oxide as in Example 1, and stirred until homogeneous. To this mixture was added 20.3 grams of di-(n-propyl)amine( $Pr_2NH$ ), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



50

The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 200°C at autogenous pressure for 24 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at room temperature.

55 Chemical analysis of the reaction solids showed 5.1 wt. % C, 1.00 wt. % N, 37.6 wt. %  $Al_2O_3$ , 51.6 wt. %  $P_2O_5$ , 10.4 wt. % LOI, giving a product composition in molar oxide ratios of:



60 The above product, denominated AlPO<sub>4</sub>-11, had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing.

**O 043 562**

	2θ	d	100×I/I <sub>0</sub>
5	8.15	10.85	34
	9.5	9.31	49
	13.3	6.66	16
	15.7	5.64	30
	16.35	5.42	5
	19.0	4.67	6
10	20.55	4.32	50
	21.0	4.23	100
	22.2	4.00	58
	22.65	3.93	75
	23.25	3.83	67
15	24.6	3.62	10
	24.8	3.59	11
	26.4	3.38	13
	26.7	3.34	17
	28.5 (sh)*	3.13 }	15
20	28.7	3.11 }	
	29.2	3.06	6
	29.6	3.02	9
	31.5	2.84	10
	33.0	2.71	15
	34.3	2.61	11
25	35.8	2.51	3
	36.6	2.46	6
	37.6 (sh)*	2.39 }	14
	37.9	2.37 }	
	39.6	2.28	4
30	40.5	2.23	2
	42.9	2.11	5
	44.8	2.02	2
	45.2	2.01	4
	46.1	1.99	6
35	48.1	1.89	2
	49.0	1.86	4
	50.6	1.80	3
	54.8	1.68	4

40 \*sh=shoulder

(b) A portion of a solid crystalline product exhibiting an X-ray powder diffraction pattern essentially identical to that above was calcined in air at about 200°C for 2 hours, then at 600°C overnight. The calcined product had an X-ray powder diffraction pattern characterized by the following data:

	2θ	d	100×I/I <sub>0</sub>
50	8.0	11.1	14
	9.8	9.03	40
	11.7	7.56	3
	12.75	6.94	20
	13.65	6.49	6
	14.7	6.03	5
55	16.1	5.50	54
	17.55	5.05	2
	19.5 (sh)	4.55	17
	19.85	4.47	23
	20.7	4.29	8
60	21.9	4.06	100
	22.1 (sh)	4.02	44
	22.5 (sh)	3.95	48
	23.5	3.79	54
	24.0 (sh)	3.71	16
65	24.2 (sh)	3.68	10

**O 043 562**

	2θ	d	100xI/I <sub>0</sub>
5	25.7	3.47	20
	25.9 (sh)	3.44	9
	26.7	3.34	13
	27.3 (sh)	3.27	14
	27.65	3.23	20
	28.5	3.13	8
10	29.6	3.02	29
	30.3	2.95	16
	31.75	2.82	8
	32.6	2.75	22
	33.95	2.64	7
	34.4 (sh)	2.61	5
15	35.5	2.53	9
	37.2	2.42	8
	38.2 (sh)	2.36	6
	38.8	2.32	14
	39.4	2.29	2
	39.7	2.27	2
20	41.0	2.20	8
	41.4 (sh)	2.18	5
	43.6	2.08	3
	44.6	2.03	5
	45.3	2.00	6
	49.2 }	1.85	8
25	49.6 }	1.84	
	50.4	1.81	3
	52.4	1.75	1
	53.6	1.71	5
	54.6	1.68	2

(sh=shoulder)

**35 Examples 33—36**

**Preparation of AlPO<sub>4</sub>-11**

A procedure similar to that in example 32 was followed except where indicated in Table C below. The composition of each final reaction mixture in molar oxide ratios was:

40



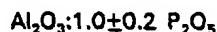
The solid product from each reaction contained in each case a phase characterized by an X-ray powder diffraction pattern essentially the same as that of the uncalcined product of example 32.

45

TABLE C

	Example #	R	Reaction time (hrs.)	Reaction
50	33	(i-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NH	24	200
	34	(C <sub>2</sub> H <sub>5</sub> )(n-C <sub>4</sub> H <sub>9</sub> )NH	24	200
	35	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NH	48	200
	36	(n-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NH	24	200
	37	(n-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NH	24	150

55 The species AlPO<sub>4</sub>-11 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



60 and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 8 below:

65

**O 043 562**

TABLE 8

	2θ	d	100xI/I <sub>0</sub>
5	9.4 — 9.5	9.41—9.31	31—49
	20.5 — 20.6	4.33—4.31	34—53
	21.0 — 21.25	4.23—4.19	100
	22.15—22.25	4.01—4.00	12—58
	22.5 — 22.7	3.95—3.92	47—75
	23.15—23.5	3.84—3.79	10—68

All of the AlPO<sub>4</sub>-11 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 9 below:

TABLE 9

	2θ	d	100xI/I <sub>0</sub>
15	8.1 — 8.2	10.9 — 10.8	19—34
	8.5 — 8.5	10.4	(sh)
	9.4 — 9.5	9.41—9.31	49—31
	13.2 — 13.3	6.71—6.66	11—16
	15.7 — 15.8	5.64—5.61	16—30
	16.3 — 16.4	5.44—5.40	3—5
19.0 — 19.2	4.67—4.62	4—7	
20.5 — 20.6	4.33—4.31	34—53	
21.0 — 21.25	4.23—4.19	100	
22.15—22.25	4.01—4.00	12—58	
22.5 — 22.7	3.95—3.92	47—75	
23.15—23.5	3.84—3.79	10—68	
24.6 — 24.8	3.62—3.59	4—10	
30	24.8 — 25.0	3.59—3.56	4—11
	26.3 — 26.4	3.39—3.38	11—18
	26.6 — 26.8	3.35—3.33	11—18
	28.3 — 28.5	3.15—3.13	(sh)
	28.7 — 28.9	3.11—3.09	11—15
35	29.1 — 29.25	3.07—3.05	5—7
	29.5 — 29.6	3.03—3.02	5—9
	31.5 — 31.6	2.84—2.83	5—10
	32.8 — 33.0	2.73—2.71	6—15
40	34.0 — 34.4	2.64—2.61	4—13
	35.6 — 35.9	2.52—2.50	2—3
	36.6 — 36.65	2.46—2.45	4—6
	37.6	2.39	12
	37.8 — 38.0	2.38—2.37	8—15
45	39.4 — 39.7	2.29—2.27	2—4
	40.5 — 40.8	2.23—2.21	2
	42.2 — 42.5	2.14—2.13	2—3
	42.7 — 43.2	2.12—2.09	4—5
	44.8 — 45.0	2.02—2.01	2—4
50	45.2 — 45.5	2.01—1.99	2—4
	46.0 — 46.2	1.97—1.96	2—6
	47.9 — 48.1	1.90—1.89	2
	48.9 — 49.1	1.86—1.86	2—4
	50.6 — 51.0	1.80—1.79	2—3
	54.8 — 54.85	1.68—1.67	2—4
55	55.5 — 55.6	1.66—1.65	2

**Example 37**

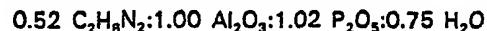
**Preparation of AlPO<sub>4</sub>-12**

A reaction mixture was prepared by combining 46.0 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 119.2 grams of water, to which was added 27.5 grams of the same hydrated aluminum oxide as in Example 1 (a pseud-boehmite phase, 74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 6.0 grams of ethylenediamine (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:

## O 043 562

The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 200°C at autogenous pressure for 24 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at room temperature.

Chemical analysis showed 4.3 wt. % C, 4.3 wt. % N, 35.0 wt. % Al<sub>2</sub>O<sub>3</sub>, 49.5 wt. % P<sub>2</sub>O<sub>5</sub>, 15.4 wt. 5 % LOI, giving a product composition in molar oxide ratios of:



The crystalline AlPO<sub>4</sub>-12 phase had an X-ray powder diffraction pattern characterized by the following data, wherein "l" is the intensity and "d" the interplanar spacing:

	2θ	d	100xl/l₀
15	6.15	14.37	25
	11.2	7.90	7
	12.3	7.20	22
	13.3	6.66	56
	14.1	6.28	5
20	15.2	5.83	4
	17.2	5.16	20
	18.5	4.80	27
	18.9	4.70	13
	19.9 (sh)	4.46	—
25	20.9	4.25	100
	22.3	3.99	44
	23.05	3.86	31
	23.85	3.73	55
	25.05	3.55	35
30	26.5	3.36	31
	26.7 (sh) }	3.34	—
	27.95 (sh) }	3.19	20
	28.2 (sh) }	3.16	—
	28.95	3.08	11
35	29.8	3.00	25
	30.4 (sh) }	2.94	—
	30.85 (sh) }	2.90	44
	31.15 (sh) }	2.87	—
	32.55	2.75	7
40	33.0 (sh) }	2.71	—
	33.2 (sh) }	2.70	5
	34.0	2.64	18
	34.8	2.58	18
	37.8	2.38	4
45	38.6	2.33	11
	39.3	2.29	9
	40.0	2.25	7
	40.7	2.22	9
	41.8	2.16	7
50	42.7 (sh)	2.12	—
	43.6	2.08	5
	44.5	2.04	5
	45.6	1.99	4
	46.6	1.95	7
55	48.15	1.89	9
	48.6	1.87	5
	50.0	1.82	5
	51.8	1.76	7
	52.7	1.74	4
60	54.6	1.68	9
	55.5	1.66	2

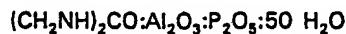
(sh=shoulder)

## O 043 562

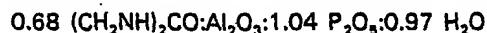
### Example 38

#### Preparation of AlPO<sub>4</sub>-12

A reaction mixture was prepared by combining 76.8 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 183.7 grams of water, to which was added 45.8 grams of the same hydrated aluminum oxide as in Example 38, and stirred until homogeneous. To this mixture was added 28.7 grams of 2-imidazolidone [(CH<sub>2</sub>NH)<sub>2</sub>CO] dissolved in 75 grams of H<sub>2</sub>O, and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:

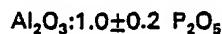


The reaction mixture was placed in a stainless steel pressure vessel having an inert liner and heated in an oven at 200°C at autogenous pressure for 169 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. Chemical analysis showed 5.2 wt. % C, 6.2 wt. % N, 33.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 48.2 wt. % P<sub>2</sub>O<sub>5</sub>, 18.1 wt. % LOI, giving a product composition in molar oxide ratios of:



The above product was AlPO<sub>4</sub>-12 as indicated by having an X-ray powder diffraction pattern essentially identical to that in Example 37.

The species AlPO<sub>4</sub>-12 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 10 below:

TABLE 10			
	2θ	d	100xl/lo
35	6.15—6.2	14.37—14.26	25—48
	13.3—13.35	6.66—6.63	56—63
	20.9—21.0	4.25—4.44	100
	22.3—22.4	3.99—3.97	33—45
	23.85—24.0	3.73—3.71	46—61
	30.85—30.95	2.90—2.89	34—44

All of the AlPO<sub>4</sub>-12 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 11 below:

TABLE 11			
	2θ	d	l/lo×100
50	6.15—6.2	14.37—14.26	48—25
	11.2—11.3	7.90—7.83	15—7
	12.3—12.35	7.20—7.17	34—22
	13.3—13.35	6.66—6.63	63—56
	14.1—14.15	6.28—6.26	8—5
	15.2	5.83	4—1
55	17.2—17.3	5.16—5.13	29—20
	18.4—18.6	4.82—4.77	37—27
	18.9	4.70	16—13
	19.9	4.46	SH
	20.9—21.0	4.25—4.23	100
	21.65—21.85	4.10—4.07	14—13
60	22.3—22.4	3.99—3.97	45—33
	22.6 SH	3.93	14
	23.0—23.05	3.87—3.86	31—9
	23.85—24.0	3.73—3.71	61—46
	25.05—25.2	3.55—3.53	35—25
	26.5—26.6	3.36—3.35	35—31
65	26.7—26.8	3.34—3.33	SH
	27.95—28.0	3.19—3.19	6—5
	28.2—28.3	3.16—3.15	SH

## O 043 562

TABLE 11 (contd.)

	$2\theta$	d	I/I <sub>0</sub> × 100
5	28.95—29.0	3.08— 3.08	13—10
	29.8 —30.0	3.00— 2.98	25—20
	30.4	2.94	SH
	30.85—30.95	2.90— 2.89	44—34
	31.1 —31.2	2.88— 2.87	SH
10	32.55—32.6	2.75— 2.75	7—6
	33.0 —33.1	2.71— 2.71	6—5
	33.2 —33.4	2.70— 2.68	SH
	34.0 —34.1	2.64— 2.63	18—17
	34.8 —34.95	2.58— 2.57	19—18
15	35.4 —35.5	2.54— 2.53	SH
	36.2	2.48	4—1
	37.0	2.43	1—0
	37.4	2.40	4—0
	37.6 —37.8	2.39— 2.38	4—0
20	37.9	2.37	SH
	38.3	2.35	SH
	38.6 —38.65	2.33— 2.33	11—8
	39.3 —39.4	2.29— 2.29	9—7
	40.0	2.25	8—7
25	40.7 —40.8	2.22— 2.21	9—7
	41.8 —41.9	2.16— 2.16	7—5
	42.6 —42.7	2.12— 2.12	SH
	43.6 —43.8	2.08— 2.07	7—5
	44.5 —44.7	2.04— 2.03	5—3
30	45.6 —45.7	1.99— 1.99	4—2
	46.5 —46.6	1.95— 1.95	7—2
	48.0 —48.15	1.90— 1.89	9—4
	48.6 —48.7	1.87— 1.87	5—4
	50.0 —50.2	1.82— 1.82	8—5
35	51.8	1.76	8—7
	52.7 — 5.29	1.74— 1.73	4—2
	54.6	1.68	9—8
	55.5	1.66	2

## Example 39

40 Preparation of AlPO<sub>4</sub>-14

(a) A reaction mixture was prepared by combining 57.7 grams of 85% orthophosphoric acid ( $H_3PO_4$ ) and 100 grams of water, to which was added 34.4 grams of a hydrated aluminum oxide (74.2 wt. %  $Al_2O_3$ , 25.8 wt. %  $H_2O$ ), and stirred until homogeneous. To this mixture was added 18.3 grams of t-butylamine ( $t-BuNH_2$ ) and then 49.1 grams of water, and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was sealed in a stainless steel pressure vessel having an inert plastic lining 50 and heated in an oven at 150°C at autogenous pressure for 96 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. Chemical analysis indicated the product contained 7.2 wt. % C, 2.6 wt. % N, 34.3 wt. %  $Al_2O_3$ , 47.7 wt. %  $P_2O_5$ , 17.5 wt. % LOI, giving a product composition in molar oxide ratios of:



The above product had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

60

65

## O 043 562

	2θ	d	100xI/I
5	9.2	9.61	100
	9.4	9.41	(sh)
	11.2	7.90	18
	13.1	6.76	17
	13.4	6.61	(sh)
	14.8	5.98	3
10	15.8	5.61	23
	18.0	4.93	12
	18.8	4.72	1
	19.2	4.62	1
	20.9	4.25	5
	21.6	4.11	10
15	22.2	4.00	22
	22.7	3.92	36
	23.4	3.80	1
	23.7	3.75	1
	25.2	3.54	2
	26.1	3.41	20
20	27.1	3.29	9
	27.7	3.22	2
	28.5	3.13	5
	29.5	3.03	12
	30.2	2.96	8
	30.5	2.93	(sh)
25	30.9	2.89	4
	31.2	2.87	(sh)
	32.0	2.80	1
	32.4	2.76	1
	33.2	2.70	(sh)
	33.5	2.67	6
30	34.1	2.63	1
	35.0	2.56	1
	35.5	2.53	2
	36.4	2.47	3
	38.1	2.36	3
	38.8	2.32	5
35	39.5	2.28	1
	40.4	2.23	5
	40.8	2.21	1
	42.0	2.15	2
	42.4	2.13	2
	43.6	2.08	1
40	44.0	2.06	3
	44.8	2.02	3
	45.9	1.98	2
	46.3	1.96	2
	47.8	1.90	2
	48.5	1.88	2
45	49.8	1.83	1
	51.6	1.77	2
	52.7	1.74	1
	53.5	1.71	4
	55	1.65	2

(sh=shoulder)

The product was designated AlPO<sub>4</sub>-14.

60 (b) A portion of the solid crystalline product obtained above was calcined in air at about 550°C for 2 hours. The calcined product had an X-ray powder diffraction pattern characterized by the following data:

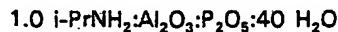
**0 043 562**

	2θ	d	100xI/Io
5	9.0	9.83	100
	9.6	9.21	(sh)
	11.5	7.69	29
	12.0	7.38	9
	13.2	6.71	45
	13.3	6.66	(sh)
10	13.6	6.51	32
	14.3	6.19	10
	14.8	5.99	5
	16.0	5.54	10
	16.2	5.47	(sh)
	16.8	5.28	2
15	18.2	4.87	35
	18.6	4.77	38
	18.9	4.70	(sh)
	19.9	4.46	5
	20.7	4.29	9
	20.9	4.25	9
20	21.6	4.11	(sh)
	22.0	4.04	23
	22.5	3.95	29
	22.8	3.90	(sh)
	23.2	3.83	7
	23.5	3.79	6
25	24.2	3.68	3
	24.8	3.59	(sh)
	25.1	3.55	6
	25.9	3.44	3
	26.6	3.35	12
	27.0	3.30	20
30	27.4	3.25	16
	27.8	3.21	11
	28.0	3.19	11
	28.6	3.12	(sh)
	29.2	3.06	11
	29.7	3.01	20
35	30.4	2.94	14
	31.0	2.88	9
	32.3	2.77	4
	33.0	2.71	6
	33.9	2.64	4
	34.8	2.58	4
40	35.6	2.52	2
	36.8	2.44	5
	37.7	2.39	3
	38.4	2.34	2
	39.1	2.30	3
	40.1	2.25	3
45	40.6	2.22	3
	41.8	2.16	1
	42.6	2.12	3
	43.0	2.10	2
	44.2	2.05	6
	45.3	2.00	1
50	46.2	1.95	2
	47.4	1.92	2
	48.6	1.87	3
	50.0	1.82	3
	52.1	1.76	3
	54.1	1.70	4

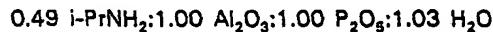
## 0 043 562

**Example 40**  
**Preparation of AlPO<sub>4</sub>-14**

A reaction mixture was prepared by combining 46.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 119.2 grams of water, to which was added 27.5 grams of the same hydrated aluminum oxide as in Example 27 and stirred until homogeneous. To this mixture was added 11.8 grams of isopropylamine (i-PrNH<sub>2</sub>), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:

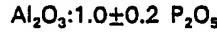


The reaction mixture was sealed in a stainless steel pressure vessel lined with an inert plastic material (polytetrafluoroethylene) and heated in an oven at 200°C at autogenous pressure for 24 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at room temperature. Chemical analysis of the product showed 6.0 wt. % C, 2.4 wt. % N, 34.8 wt. % Al<sub>2</sub>O<sub>3</sub>, 48.6 wt. % P<sub>2</sub>O<sub>5</sub>, 16.1 wt. % LOI, giving a product composition in molar oxide ratios of:



The above product was established to be AlPO<sub>4</sub>-14 by virtue of having an X-ray powder diffraction pattern essentially identical to that of the uncalcined product in Example 39.

The species AlPO<sub>4</sub>-14 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 12 below:

TABLE 12			
	2θ	d	100x1/I <sub>0</sub>
30	8.9 — 9.2	9.94—9.61	100—>100
	11.1 — 11.2	7.97—7.90	18—28
	13.05—13.1	6.78—6.76	17—23
	15.8 — 15.85	5.61—5.59	21—23
	22.2 — 22.3	4.00—3.99	22—28
	22.7	3.92	36—49
	26.1 — 26.2	3.44—3.40	20—25

All of the AlPO<sub>4</sub>-14 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 12(a) below:

TABLE 12(a)			
	2θ	d	100x1/I <sub>0</sub>
45	8.9 — 9.2	9.94—9.61	100—<100
	9.4	9.41	(sh)
	11.1—11.2	7.97—7.90	18—28
	13.1	6.76	17—23
	13.4	6.61	(sh)—9
	14.8	5.98	3
	15.8—15.85	5.61—5.59	21—23
50	18.0	4.93	12—20
	18.8	4.72	1—2
	19.2	4.62	1
	20.9	4.25	5—10
	21.6—21.9	4.11—4.06	5—10
	22.2—22.3	4.00—3.99	22—28
	22.7	3.92	36—49
55	23.4	3.80	1
	23.7—23.85	3.75—3.73	1—2
	25.2—25.45	3.54—3.50	2—4
	26.1—26.2	3.41—3.40	20—25
	27.1—27.2	3.29—3.28	6—9
	27.7	3.22	2—4

## O 043 562

TABLE 12(a) (contd.)

	2θ	d	100×I/I <sub>0</sub>
5	28.5—28.85	3.13—3.09	(sh)—5
	29.5—29.6	3.03—3.02	12—20
	30.2—30.3	2.96—2.95	8—11
	30.5	2.93	(sh)
10	30.9	2.89	4—18
	31.2—31.3	2.87—2.86	(sh)
	32.0—32.2	2.80—2.78	1—3
	32.4—32.6	2.76—2.75	1—3
	33.2—33.3	2.70—2.69	(sh)—3
	33.5—33.8	2.67—2.65	6—8
15	34.1	2.63	1
	35.0—35.2	2.56—2.55	1—3
	35.5—35.7	2.53—2.51	2—5
	36.4—36.6	2.47—2.46	3—4
	37.3	2.41	1
	38.0—38.1	2.37—2.36	1—3
20	38.5—38.8	2.34—2.32	2—5
	39.1—39.5	2.30—2.28	(sh)—4
	40.4—40.5	2.23—2.23	4—5
	40.8—41.0	2.21—2.20	2—4
	42.4	2.13	2—3
25	42.8	2.11	2
	43.6	2.08	1
	44.0—44.2	2.06—2.05	3
	44.6—44.8	2.03—2.02	3
30	45.0	2.01	3
	45.9	1.98	2
	46.2—46.3	1.96—1.96	2
	46.6	1.95	3
35	47.8—48.0	1.90—1.90	2—3
	48.5—48.7	1.88—1.87	2—3
	49.8—50.0	1.83—1.82	1—2
	51.6—52.0	1.77—1.76	2—3
40	52.7—52.8	1.73—1.74	1—2
	53.5—54.1	1.71—1.70	4
	55.2—55.7	1.66—1.65	1—2

(sh=shoulder)

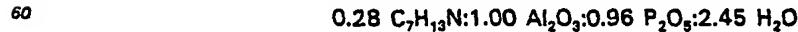
## Example 41

Preparation of AlPO<sub>4</sub>-16

45 (a) A reaction mixture was prepared by combining 57.7 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 69.6 grams of water, to which was added 34.4 grams of a hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 27.8 grams of quinuclidine (C<sub>7</sub>H<sub>13</sub>N) dissolved in 50.4 grams of water, and then 29.1 grams of water and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



55 The reaction mixture was sealed in a stainless steel pressure vessel lined with an inert plastic material and heated in an oven at 150°C at autogenous pressure for 48 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. Chemical analysis of the product indicated the presence of 7.6 wt. % C, 1.33 wt. % N, 32.4 wt. % Al<sub>2</sub>O<sub>3</sub>, 43.4 wt. % P<sub>2</sub>O<sub>5</sub>, 24.1 wt. % LOI, giving a product composition in molar oxide ratios of:



The above product had an X-ray powder diffraction pattern characterized by the following data wherein "I" is the intensity and "d" the interplanar spacing:

## O 043 562

	2θ	d	100xI/I <sub>0</sub>
5	11.3	7.83	62
	15.5	5.72	2
	17.3	5.13	2
	18.7	4.75	50
	21.9	4.06	100
	22.95	3.875	9 (sh)
10	26.55	3.357	27
	27.6	3.23	2
	28.0	3.19	2
	29.0	3.08	12
	29.75	3.00	28
	32.7	2.739	4
15	34.7	2.585	5
	37.9	2.374	8
	39.6	2.276	2
	44.2	2.049	2
	48.5	1.877	6
	52.4	1.746	3
20	54.8	1.675	3

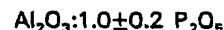
The product was designated AlPO<sub>4</sub>-16.

(b) Using the same procedure and reaction mixture composition as in part (a) except that the proportion of quinuclidine was decreased by 50 percent and the mixture was heated at 200°C for 24 hours, AlPO<sub>4</sub>-16 was again produced. A small amount of AlPO<sub>4</sub>-17 was also present as an impurity.

(c) The procedure and gel composition of part (a) were followed except that the reaction mixture was heated for 16 hours. A portion of the solids was submitted for X-ray analysis. The above product was established to be AlPO<sub>4</sub>-16 by virtue of having a powder diffraction pattern essentially identical with that in part (a).

(d) A portion of the solid crystalline product obtained above was calcined in air from 200°C to 500°C during 1 hour and then at about 500°C for 2 hours. The calcined product had an X-ray powder diffraction pattern essentially identical to that in part (c).

The species AlPO<sub>4</sub>-16 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 13 below:

	2θ	d	100xI/I <sub>0</sub>
45	11.3—11.5	7.83—7.69	59—63
	18.7—18.85	4.75—4.71	48—54
	21.9—22.2	4.06—4.00	100
	26.55—26.75	3.36—3.33	23—27
	29.75—29.95	3.00—2.98	26—30

All of the AlPO<sub>4</sub>-16 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 14 below:

55

60

65

## O 043 562

TABLE 14

 $2\theta$ 

d

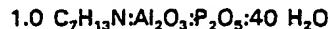
100*x**I/I<sub>0</sub>*

	$2\theta$	d	$100xI/I_0$
5	11.3 —11.5	7.83 —7.69	59—63
	15.5 —15.9	5.72 —5.57	0—2
	17.3 —17.4	5.13 —5.10	0—2
	18.7 —18.85	4.75 —4.71	48—54
	21.9 —22.2	4.06 —4.00	100
	22.95—23.1	3.875—3.850	9—11
10	26.55—26.75	3.357—3.332	23—27
	27.4 —27.6	3.255—3.232	0—2
	28.0 —28.2	3.187—3.164	0—2
	29.0 —29.1	3.079—3.058	8—15
	29.75—29.95	3.003—2.983	26—30
	32.7 —32.9	2.739—2.722	4—5
15	34.7 —34.95	2.585—2.567	5—7
	37.9 —38.1	2.374—2.362	8—10
	39.6 —40.0	2.276—2.254	0—2
	44.2 —44.5	2.049—2.036	2—3
	48.5 —48.7	1.877—1.870	6—8
	52.4 —52.6	1.746—1.740	2—3
20	54.8 —55.0	1.675—1.670	2—3

## Example 42

25 Preparation of AlPO<sub>4</sub>-17

(a) A reaction mixture was prepared by combining 56.7 grams of 85% orthophosphoric acid ( $H_3PO_4$ ) and 69.6 grams of water, to which was added 34.4 grams of a hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt. %  $Al_2O_3$ , 35.8 wt. %  $H_2O$ ), and stirred until homogeneous. To this mixture was added 27.8 grams of quinuclidine ( $C_7H_{13}N$ ) dissolved in 50.4 grams of water, and then 30 29.1 grams of water, and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



35 The reaction mixture was placed in a sealed stainless steel pressure vessel lined with an inert plastic material (polytetrafluoroethylene) and heated in an oven at 200°C at autogenous pressure for 96 hours. The solid reaction product was recovered and washed by repeated centrifugation with water, and dried in air at 110°C. Chemical analysis showed 12.4 wt. % C, 2.2 wt. % N, 32.5 wt. %  $Al_2O_3$ , 45.9 wt. %  $P_2O_5$ , 21.4 wt. % LOI, giving a product composition in molar oxide ratios of:



The above product, denominated AlPO<sub>4</sub>-17 had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:  
45

50

55

60

65

**O 043 562**

	2θ	d	100xI/I
5	7.65	11.55	100
	9.7	9.12	41
	11.35	7.79	2
	11.9	7.44	3
	13.35	6.63	39
	14.2	6.24	13
	14.7	6.03	2
	15.4	5.75	62
	16.6	5.34	33
10	18.0	4.93	20
	18.8	4.72	2
	19.6	4.53	67
	20.5	4.33	93
	21.4	4.15	50
	22.1	4.02	2
	22.5	3.95	15
	23.3	3.82	34
	23.8	3.74	39
20	24.2	3.68	3
	25.3	3.52	55
	26.95	3.38	35
	27.4	3.26	20
	28.05	3.18	5
	28.7	3.11	20
	30.6	2.92	17
	31.2	2.87	29
	31.8	2.81	68
30	32.4	2.76	2
	33.5	2.67	18
	34.0	2.64	2
	34.6	2.59	2
	35.15	2.55	2
	35.9	2.50	7
	36.4	2.47	6
	36.8	2.44	2
	37.3	2.41	2
40	38.0	2.37	3
	39.4	2.29	2
	39.8	2.26	7
	40.4	2.23	4
	41.2	2.19	3
	42.2	2.14	3
	42.8	2.11	1
	43.6	2.08	9
	44.45	2.04	2
50	45.75	1.98	5
	46.2	1.96	1
	46.6	1.95	4
	47.8	1.90	3
	48.6	1.87	2
	49.25	1.85	8
	49.65	1.84	11
	50.2	1.82	2
	51.25	1.78	1
55	52.0	1.76	11
	53.2	1.72	1
	53.85	1.70	5
	55.45	1.66	8

(b) A portion of the solid crystalline product obtained after continuing the digestion of the above reaction mixture to 168 hours exhibited an X-ray powder diffraction pattern essentially identical to that above.

**O 043 562**

(c) A portion of the product from part (b) calcined in air at about 550°C for 2 hours. The calcined product had an X-ray powder diffraction pattern characterized by the following data:

	2θ(°)	d(A)	100xI/I₀
5	7.7	11.5	77
	9.7	9.1	46
	11.6	7.63}	
	11.85	7.47}	13
10	13.45	6.58	100
	14.0	6.33	21
	14.2	6.24	28
	14.8	5.99	2
	15.6	5.68	16
15	16.8	5.28	6
	18.0	5.22	3
	19.2	4.62	5
	19.65	4.52	12
	20.5	4.33}	
20	20.8	4.27}	42
	21.6	4.11	22
	22.2	4.00	2
	22.6	3.93	2
	23.65	3.76}	
25	23.95	3.72}	29
	24.4	3.65}	
	24.6	3.63}	22
	25.0	3.56	7
	25.3	3.52	12
30	26.2	3.40	7
	27.3	3.26	20
	28.2	3.16	15
	28.8	3.10	10
	29.4	3.038}	
35	29.6	3.018}	7
	30.1	2.969	7
	30.8	2.903	7
	31.4	2.849	24
	31.9	2.805}	
40	32.1	2.788}	15
	33.7	2.660	11
	35.2	2.550	1
	36.1	2.488}	
	36.35	2.471}	7
45	39.6	2.281	2
	41.3	2.186	3
	42.0	2.151	2
	42.7	2.118	4
	43.8	2.067	1
50	44.9	2.019	1
	46.1	1.973	1
	46.6	1.953	2
	47.4	1.972	3
	48.0	1.895	2
55	49.2	1.852	2
	50.2	1.817	7
	51.3	1.781	7
	52.8	1.734	2
	54.0	1.698	1
60	55.3	1.661	2

**Example 43**  
**Preparation of AlPO<sub>4</sub>-17**

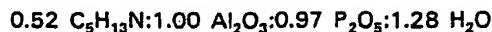
A reaction mixture was prepared by combining 115.3 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>)  
65 and 256 grams of water, to which was added 68.7 grams of a hydrated aluminum oxide (a pseudo-

## O 043 562

boehmit phase, 74.2 wt. %  $\text{Al}_2\text{O}_3$ , 25.8 wt. %  $\text{H}_2\text{O}$ , and stirred until homogeneous. To this mixture was added 43.6 grams of neopentylamine ( $\text{C}_5\text{H}_{13}\text{N}$ ) and then 44.1 grams of water, and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was placed in a stainless steel pressure vessel lined with an inert plastic material (polytetrafluoroethylene) and heated in an oven at 150°C at autogenous pressure for 168 hours. The solid reaction product was recovered and washed by repeated centrifugation with water, 10 and dried in air at 110°C. Chemical analysis showed 9.9 wt. % C, 2.5 wt. % N, 32.6 wt. %  $\text{Al}_2\text{O}_3$ , 44.2 wt. %  $\text{P}_2\text{O}_5$ , 21.8 wt. % LOI, giving a product composition in molar oxide ratios of:



15 The major phase in the above product had an X-ray powder diffraction pattern very similar to that of the product in Example 42(a). The product was designated  $\text{AlPO}_4$ -17.

### Examples 44—45

#### Preparation of $\text{AlPO}_4$ -17

20 A procedure similar to that in Example 42 was followed except where indicated in Table D. The composition of each final reaction mixture in molar-oxide ratios was:

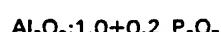


25 where R is indicated in Table D. A portion of the solid product from each reaction was subjected to X-ray analysis and in each case a phase characterised by an X-ray powder diffraction pattern essentially the same as that of the product of Example 42(a) was observed.

TABLE D

30	Example #	R	Reaction time (hrs)	Reaction temp (°C)
	44	Cyclohexylamine	168	200
	45	Piperidine	168	200

35 The species  $\text{AlPO}_4$ -17 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



40 and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 15 below:

TABLE 15  
d

45	2θ	d	100xl/lo
	7.6 — 7.8	11.6 — 11.33	100
	13.25 — 13.5	6.68 — 6.56	39—54
	15.35 — 15.6	5.77 — 5.68	26—62
50	19.55 — 19.75	4.54 — 4.50	14—67
	20.35 — 20.65	4.36 — 4.30	45—93
	21.25 — 21.5	4.18 — 4.13	20—50
	25.3 — 25.45	3.52 — 3.50	12—55
	31.65 — 31.85	2.83 — 2.81	19—68

55 All of the  $\text{AlPO}_4$ -17 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 16 below:

60

65

## O 043 562

TABLE 16

 $2\theta$ 

d

100xI/I

5	7.6 — 7.8	11.6 — 11.33	100
	9.7 — 9.9	9.12 — 8.93	15—41
	11.35—11.9	7.80 — 7.44	4—5
	13.25—13.5	6.68 — 6.56	39—54
	14.2 — 14.4	6.24 — 6.15	2—13
10	15.35—15.6	5.77 — 5.68	26—62
	16.5 — 16.7	5.37 — 5.31	10—33
	17.9 — 18.15	4.96 — 4.89	4—20
	19.55—19.75	4.54 — 4.50	14—67
	20.35—20.65	4.36 — 4.30	45—93
15	21.25—21.5	4.18 — 4.13	20—50
	21.7 — 21.8	4.10 — 4.08	(sh)
	22.5 — 22.65	3.95 — 3.93	3—15
	23.1 — 23.45	3.85 — 3.79	17—34
	23.7 — 23.95	3.75 — 3.72	14—39
20	24.1 — 24.2	3.69 — 3.68	(sh)
	25.3 — 25.45	3.52 — 3.50	12—55
	26.75—27.0	3.33 — 3.30	14—35
	27.35—27.5	3.26 — 3.24	5—20
	27.85—28.2	3.20 — 3.16	2—5
25	28.6 — 28.8	3.12 — 3.10	5—20
	29.45—29.8	3.03 — 3.00	2—1
	30.45—30.7	2.94 — 2.91	4—17
	31.0 — 31.3	2.88 — 2.86	13—29
	31.65—31.85	2.83 — 2.81	19—68
30	32.3 — 32.4	2.77 — 2.76	1—2
	33.4 — 33.6	2.68 — 2.67	18—8
	34.0	2.64	2
	34.6	2.59	2
	35.15	2.55.	2
35	35.7 — 36.0	2.51 — 2.49	4—7
	36.3 — 36.6	2.47 — 2.45	1—6
	36.8	2.44	2
	37.3	2.41	2
	37.8 — 38.0	2.38	1—3
40	39.2 — 39.4	2.30	2
	39.65—39.9	2.27 — 2.26	2—7
	40.3 — 40.5	2.24 — 2.23	1—4
	41.0 — 41.2	2.20 — 2.19	1—3
	41.9 — 42.2	2.16 — 2.14	1—3
45	42.8	2.11	1
	43.6 — 43.8	2.08 — 2.07	2—9
	44.45	2.04	2
	45.5 — 45.8	1.99 — 1.98	1—5
	46.2	1.97	1
50	46.5 — 46.7	1.95 — 1.95	1—4
	47.35—47.8	1.92 — 1.90	1—3
	48.55—48.8	1.88 — 1.87	1—2
	49.25	1.85	8
	49.45—49.7	1.84 — 1.83	4—11
55	50.2 — 50.25	1.82 — 1.82	1—2
	51.25	1.78	1
	52.0 — 52.2	1.76 — 1.75	3—11
	53.1 — 53.2	1.72 — 1.72	1
	53.75—54.0	1.71 — 1.70	1—5
60	55.2 — 55.5	1.66 — 1.66	3—8
	(sh=should r)		

## Example 46

Preparation of AlPO<sub>4</sub>-18

A reaction mixture was prepared by combining 46.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 53.8 grams of water, to which was added 27.5 grams of a pseudo-boehmit phase, (74.2 wt. %

## 0 043 562

$\text{Al}_2\text{O}_3$ , 25.8 wt. %  $\text{H}_2\text{O}$ ), and stirred until homogeneous. To this mixture was added an aqueous solution prepared by combining 6.5 grams of 37 wt. % HCl and 98.0 grams of 40 wt. % tetraethylammonium hydroxide (TEAOH), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:

$$5 \quad 0.33 \text{ HCl}:0.67 (\text{TEA})_2\text{O}:\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:40 \text{ H}_2\text{O}$$

The reaction mixture was placed in a sealed stainless steel pressure vessel lined with an inert plastic material (polytetrafluoroethylene) and heated in an oven at 150°C at autogenous pressure for 336 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 10 room temperature. Chemical analysis showed 8.9 wt. % C, 1.28 wt. % N, 33.5 wt. %  $\text{Al}_2\text{O}_3$ , 38.9 wt. %  $\text{P}_2\text{O}_5$ , 26.4 wt. % LOI, giving a product composition in molar oxide ratios of:

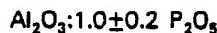
$$0.14 (\text{TEA})_2\text{O}:1.00 \text{ Al}_2\text{O}_3:0.83 \text{ P}_2\text{O}_5:0.9 \text{ H}_2\text{O}$$

15 The above product contained a minor amount of crystalline impurity but the major phase, denominated  $\text{AlPO}_4\text{-18}$ , had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

	2θ	d	100×I/I₀
20	9.60	9.21	100
	10.45	8.47	8
	11.0	8.04	9
	13.1	6.76	6
	14.0	6.33	8
25	14.8	5.99	10
	15.5	5.72	27
	16.9}	5.25	
	17.0}	5.22	61
	17.9	4.96	20
30	19.3}	4.60	17
	19.5}	4.55	
	20.15	4.41	35
	20.95	4.24	45
	22.1}	4.02	
35	22.3}	3.99	17
	23.3	3.82	5
	23.85	3.73	6
	24.4	3.65	14
	24.9	3.58	9
40	25.4	3.51	6
	26.1	3.41	13
	26.45}	3.37	
	26.8}	3.33	12
	28.0	3.19	16
45	29.0	3.08	7
	30.0	2.98	20
	30.75	2.91	14
	31.3	2.86	14
	31.8}	2.81	
50	32.4}	2.76	24
	33.4	2.68	6
	34.5	2.60	3
	35.8}	2.51	
	36.2}	2.48	3
55	38.2	2.36	2
	40.2	2.24	1
	41.7	2.17	3
	42.9	2.11	5
	47.8	1.90	3
60	48.6	1.87	2
	49.6	1.84	4
	51.0	1.79	4
	52.0	1.76	2
	54.2	1.69	4
65	55.1	1.67	2

## O 043 562

The species AlPO<sub>4</sub>-18 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



5

and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 17 below:

	2θ	d	100xi/lo
10	9.60—9.65	9.21—9.	100
	15.5 —15.55	5.72—5.70	27—34
	16.9 —17.1	5.25—5.19	61—70
15	17.9	4.96	20—25
	20.15—20.25	4.41—4.39	35—43
	20.95—21.05	4.24—4.22	45—52
	30.0 —30.1	2.98—2.97	20—25
20	31.8 —32.5	2.81—2.75	24—27

All of the AlPO<sub>4</sub>-18 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 18 below:

	2θ	d	100xi/lo
25	9.60—9.65	9.21—9.17	100
	10.45—10.50	8.47—8.42	8
	11.0 —11.05	8.04—8.01	9—12
30	13.1 —13.2	6.76—6.71	6—7
	14.0	6.33	8
	14.8 —14.85	5.99—5.97	10—11
	15.5 —15.55	5.72—5.70	27—34
	16.9 —17.1	5.25—5.19	61—70
35	17.9	4.96	20—25
	19.35—19.6	4.59—4.53	8—17
	20.15—20.25	4.41—4.39	35—43
	20.95—21.05	4.27—4.22	45—52
40	22.1 —22.3	4.02—3.99	17—19
	23.3 —23.4	3.82—3.80	5—7
	23.85—24.0	3.73—3.71	6—8
	24.4 —24.5	3.65—3.63	14
	24.9 —25.0	3.58—3.56	9—11
45	25.4 —25.55	3.51—3.49	6—7
	26.1 —26.2	3.41—3.40	13—15
	26.45—26.9	3.37—3.31	12
	28.0 —28.2	3.19—3.16	16—17
50	30.0 —30.1	3.98—3.97	20—25
	30.75—30.9	2.91—2.87	14—17
	31.3 —31.4	2.86—2.85	14—15
	31.8 —32.5	2.81—2.75	24—27
	33.3 —33.55	2.69—2.67	6
55	34.5 —34.6	2.60—2.59	3—4
	35.8 —36.2	2.51—2.48	3—4
	40.0 —40.2	2.25—2.24	1—2
	41.7 —41.8	2.17—2.16	2—3
60	42.9 —43.0	2.11—2.10	5
	47.8	1.90	3—4
	49.6	1.84	4—5
	51.0	1.79	4—7
	52.0	1.76	2—4
	54.2 —54.4	1.69—1.69	3—4

(b) A portion of the solid crystalline product obtained from a similar preparation and exhibiting an  
65 X-ray powder diffraction pattern essentially identical to that of part (a) was calcined stepwise in 100°

## O 043 562

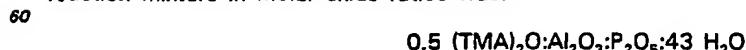
increments from 100° to 600°C, being held at each temperature for one hour before the next increment. The calcined product had an X-ray powder diffraction pattern characterized by the following data:

<b>5</b>	<b>2θ</b>	<b>d</b>	<b>100xI/I<sub>0</sub></b>
<b>10</b>	9.5	9.31	100
	10.0	8.85	sh
	10.4	8.51	sh
	10.6	8.35	14
	11.3	7.83	4
	12.95	6.83	9
	13.5	6.56	8
<b>15</b>	14.5	6.11	4
	16.1	5.50	11
	17.0	5.22	18
	17.2	5.16	17
	19.1	4.65	5
	19.7	4.51	7
	20.0	4.44	6
<b>20</b>	20.7	4.29	12
	21.3	4.17	15
	21.9	4.06	5
	22.5	3.95	8
	22.9	3.88	9
	23.9	3.72	12
	24.3	3.66	sh
<b>25</b>	24.9	3.58	3
	25.2	3.53	3
	25.7	3.47	sh
	26.0	3.43	8
	26.3	3.39	7
	27.1	3.29	4
	27.8	3.21	7
<b>35</b>	29.1	3.07	7
	30.0	2.98	8
	30.4	2.94	sh
	31.0	2.88	13
	31.6	2.83	5
	32.2	2.78	7
	32.6	2.75	sh
<b>40</b>	33.0	2.71	sh
	33.7	2.66	4
	34.7	2.59	3
	37.0	2.43	2
	38.8	2.32	2
	43.2	2.09	2
	49.0	1.86	4
<b>50</b>	55.2	1.66	3
	55.8	1.65	2

### Example 47

#### Preparation of AlPO<sub>4</sub>-20

(a) A reaction mixture was prepared by combining 23.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 34.6 grams of water, to which was added 13.8 grams of a hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 36.2 grams of tetramethylammonium hydroxide pentahydrate (TMAOH · 5H<sub>2</sub>O) dissolved in 50 grams of H<sub>2</sub>O and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 150°C at autogenous pressure for 71 hours. The solid reaction product was recovered by repeated centrifugation and washing with water, and dried in air at room

## O 043 562

temperature. Chemical analysis of the product showed 6.0 wt. % C, 1.76 wt. % N, 32.7 wt. % Al<sub>2</sub>O<sub>3</sub>, 44.8 wt. % P<sub>2</sub>O<sub>5</sub>, 22.8 wt. % LOI, giving a product composition in molar oxide ratios of:



5

The AlPO<sub>4</sub>-20 product contained a minor amount of crystalline impurity, but the major phase had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

	2θ	d	100×I/I <sub>0</sub>
10	14.0	6.326	51
	19.9	4.462	44
	22.3	3.986	16
	24.5	3.633	100
	28.2	3.164	25
	31.6	2.831	18
15	34.7	2.585	18
	40.3	2.238	4
	43.1	2.099	5
	47.8	1.903	4
	52.2	1.752	10

(b) A portion of the solid crystalline product obtained from a similar preparation and exhibiting an X-ray powder diffraction pattern essentially identical to that of part (a) was calcined in air at about 100°C for 1 hour, 200°C for 1 hour, 400°C for 1 hour and finally at 620°C for 1 hour. The calcined product had an X-ray powder diffraction pattern characterized by the following data:

	2θ	d	100×I/I <sub>0</sub>
30	14.3	6.19	100
	20.3	4.37	27
	22.7	3.92	9
	24.8	3.59	57
	28.4	3.14	20
	32.1	2.79	19
35	35.1	2.56	13
	40.9	2.21	4
	52.7	1.74	6

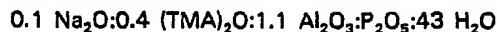
40

AlPO<sub>4</sub>-20 appears to be a structural analogue of the aluminosilicate sodalite.

### Example 48

#### Preparation of AlPO<sub>4</sub>-20

45 A reaction mixture was prepared by combining 57.6 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 90.5 grams of water, to which was added 37.8 grams of the same hydrated aluminum oxide as in Example 47 and stirred until homogeneous. To this mixture was added 36.2 grams of tetramethylammonium hydroxide pentahydrate (TMAOH · 5H<sub>2</sub>O) and 2.0 grams of sodium hydroxide dissolved in 50 grams of H<sub>2</sub>O, and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



55 The reaction mixture was placed in a sealed stainless steel pressure vessel lined with an inert plastic material and heated in an oven at 150°C. at autogenous pressure for 72 hours. The solid reaction product was recovered by centrifuging and washing with water, and dried in air at 110°C. A portion of the solids was subjected to X-ray analysis. The AlPO<sub>4</sub>-20 product had an X-ray powder diffraction pattern essentially identical to that of the uncalcined product in Example 47(a).

60 Example 49

#### Preparation of AlPO<sub>4</sub>-20

A reaction mixture was prepared by combining 92.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 220.9 grams of water, to which was added 55.0 grams of a hydrated aluminum oxide (Catapal SB, a pseudo-boehmite phase, 74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 72.5 grams of tetramethylammonium hydroxide pentahydrate (TMAOH · 5H<sub>2</sub>O)

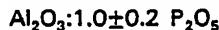
## O 043 562

dissolved in 50 grams H<sub>2</sub>O and the mixture stirred until homogeneous. To this mixture 13.0 grams of NaA zeolite were added and the mixture homogenized. Exclusive of the NaA zeolite, the composition of the final reaction mixture in molar oxide ratios was:

5                   0.5 (TMA)<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>:P<sub>2</sub>O<sub>5</sub>:50 H<sub>2</sub>O

The reaction mixture was placed in a stainless steel pressure vessel having an inert plastic lining and heated in an oven at 125°C at autogenous pressure for 53 hours. The solid reaction product was recovered by centrifuging and washing with water, and dried in air at 110°C. The AlPO<sub>4</sub>-20 product had an X-ray powder diffraction pattern essentially identical to that of the product in Example 47(a).

10                  The species AlPO<sub>4</sub>-20 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



15                  and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 19 below:

20	2θ	d	100xi/lo
25	13.9—14.1	6.37—6.28	40—55
	19.8—20.0	4.48—4.44	40—48
	24.3—24.5	3.66—3.63	100
	28.2—28.3	3.16—3.15	12—25
30	31.4—31.7	2.85—2.82	11—18
	34.6—34.8	2.59—2.58	15—18

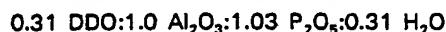
All of the AlPO<sub>4</sub>-20 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 20 below:

30	2θ	d.	100xi/lo
35	13.9—14.1	6.37—6.28	40—55
	19.8—20.0	4.48—4.44	40—48
	22.2—22.4	4.00—3.97	5—16
	24.3—24.5	3.66—3.63	100
	28.2—28.3	3.16—3.15	12—25
40	31.4—31.7	2.85—2.82	11—18
	34.6—34.8	2.59—2.58	15—18
	40.2—40.5	2.24—2.23	4—5
	42.7—43.1	2.12—2.01	5—8
	47.5—47.8	1.91—1.90	4—7
	51.9—52.2	1.76—1.75	10—11

45                  Example 50  
 Preparation of AlPO<sub>4</sub>-22  
 (a) A reaction mixture was prepared by combining 57.7 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 80.4 grams of water, to which was added 34.4 grams of a hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 110.6 grams of an aqueous solution of 68.2 wt. % N,N'-dimethyl-1,1,4-diazabicyclo(2.2.2)octane dihydroxide (DDO), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:

55                  1.7 DDO:Al<sub>2</sub>O<sub>3</sub>:P<sub>2</sub>O<sub>5</sub>:40 H<sub>2</sub>O

The reaction mixture was sealed in a lined stainless steel pressure vessel and heated in an oven at 200°C at autogenous pressure for 72 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. Chemical analysis showed 9.6 wt. % C, 2.9 wt. % N, 33.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 47.6 wt. % P<sub>2</sub>O<sub>5</sub>, 19.4 wt. % LOI, giving a product composition in molar oxide ratios:



60                  The above product, denominated AlPO<sub>4</sub>-22, had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

**O 043 562**

	2θ	d	100xI/I <sub>0</sub>
5	8.55	10.34	25
	9.0	9.83	2 (sh)
	9.1	9.72	57
	11.4	7.76	1
	12.7	6.97	(sh)
	13.0	6.81	9
10	14.6	6.07	4
	15.6	5.68	6
	17.3	5.13	26
	18.5	4.80	100
	20.65	4.30	43
	21.4	4.15	1 (sh)
15	21.75	4.08	19
	22.6	3.93	6
	23.7	3.75	22
	23.85	3.7	23
	24.2	3.68	8
	24.8	3.59	24
20	26.2	3.40	36
	27.0	3.30	(sh)
	27.3	3.27	20
	27.8	3.21	8
	28.6	3.12	10
	29.3	3.05	30
25	30.1	2.969	8
	31.55	2.835	16
	32.2	2.780	2
	33.0	2.714	2
	33.2	2.698	2
	34.15	2.625	2
30	34.9	2.571	11
	35.55	2.525	5
	37.4	2.404	(sh)
	37.6	2.392	9
	39.1	2.304	1
	39.25	2.295	1
35	39.75	2.268	2
	40.35	2.235	4
	41.2	2.191	2
	42.1	2.146	2
	43.7	2.071	1
	44.3	2.045	4
40	44.7	2.027	2
	45.2	2.006	4
	46.4	1.957	1
	47.0	1.933	2
	48.4 (sh)	1.881	4
	48.75	1.868	13
45	49.7	1.834	5
	50.2	1.817	2
	51.4	1.778	<1
	53.2	1.722	3
	54.0	1.698	5
	54.4	1.687	2

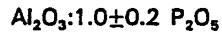
{sh=shoulder}

60 (b) A portion of the solid crystalline product obtained above was calcined in air at about 600°C for 2 hours. The calcined AlPO<sub>4</sub>-22 had an X-ray powder diffraction pattern characterized by the following data:

**O 043 562**

	2θ	d	100×I/I <sub>0</sub>
5	8.6	10.28	(sh)
	9.15	9.65	100
	12.6	7.03	
	12.9	6.86	42
	13.0	6.81	
	14.4	6.15	
10	14.7	6.03	21
	17.3	5.13	50
	18.5	4.80	92
	20.4	4.35	64
	21.55	4.12	23
	22.5	3.95	11
15	23.9	3.72	34
	24.8	3.59	18
	25.9	3.44	32
	26.1	3.41	(sh)
	27.3	3.27	24
	27.5	3.24	(sh)
20	28.4	3.14	12
	29.1	3.07	31
	31.2	2.867	
	31.4	2.849	19
	32.9	2.722	4
	34.55	2.596	15
25	34.9	2.571	14
	35.5	2.529	5
	37.3	2.411	3
	39.6	2.275	1
	40.8	2.212	3
	41.5	2.176	1
30	44.4	2.040	4
	44.9	2.019	2
	46.7	1.945	3
	47.2	1.926	2
	47.8	1.903	3
	48.2	1.888	3
35	49.0	1.859	2
	52.7	1.737	2
	53.4	1.716	4

The species AlPO<sub>4</sub>-22 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is  
45



and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 21 below:  
50

TABLE 21:

	2θ	d	100×I/I <sub>0</sub>
55	9.1 — 9.15	9.72—9.66	57—100
	18.45—18.5	4.81—4.80	66—100
	20.55—20.65	4.32—4.30	43—70
	26.1 —26.2	3.41—3.40	36—44
	29.3	3.05	30—32
	31.55	2.835	16—29

All of the AlPO<sub>4</sub>-22 compositions for which the X-ray powder diffraction data has presently been obtained have patterns that are within the generalized pattern of Table 22 below:  
60

## O 043 562

TABLE 22

2θ

d

100×I/I<sub>0</sub>

5	8.55	10.34	15—25
	9.0	9.83	(sh)
	9.1 — 9.15	9.72 — 9.66	57—100
	11.4	7.76	0—1
	12.7	6.97	(sh)
10	12.95—13.0	6.83 — 6.81	9—14
	14.5 — 14.6	6.11 — 6.07	3—5
	15.55—15.6	5.70 — 5.68	4—6
	17.25—17.3	5.14 — 5.13	22—26
	18.45—18.5	4.81 — 4.80	66—100
	20.55—20.65	4.32 — 4.30	43—70
15	21.65—21.75	4.10 — 4.09	12—19
	22.6	3.93	6—7
	23.6 — 23.7	3.77 — 3.75	22
	23.8 — 23.85	3.74 — 3.73	18—23
	24.2	3.68	8—14
	24.7 — 24.8	3.60 — 3.59	10—24
20	26.1 — 26.2	3.41 — 3.40	36—44
	27.0	3.30	(sh)
	27.2 — 27.3	3.28 — 3.27	17—20
	27.7 — 27.8	3.22 — 3.21	8—23
	28.6	3.12	10—14
	29.3	3.05	30—32
25	30.1	2.969	6—8
	31.55	2.835	16—29
	32.2	2.780	0—2
	32.9 — 33.0	2.722—2.714	2—3
	33.2 — 33.3	2.698—2.691	2—3
	34.1 — 34.15	2.629—2.625	2—3
30	34.9	2.571	5—11
	35.55	2.525	5—8
	37.4	2.404	(sh)
	37.5 — 37.6	2.398—2.392	6—9
	39.0 — 39.25	2.309—2.295	1—2
	39.75	2.267	0—2
35	40.30—40.35	2.238—2.235	2—3
	41.0 — 41.2	2.201—2.191	1—2
	41.9 — 42.1	2.156—2.146	2—3
	43.7	2.071	1—5
	44.2 — 44.3	2.049—2.045	3—4
	44.7 — 44.9	2.027—2.019	1—2
40	45.2 — 45.3	2.006—2.002	<1—4
	46.2 — 46.4	1.965—1.957	<1—1
	46.8 — 47.0	1.941—1.933	<1—2
	48.1 — 48.4	1.892—1.881	(sh)—6
	48.6 — 48.75	1.873—1.868	13—19
	49.6 — 49.7	1.838—1.834	4—5
45	50.1 — 50.2	1.821—1.817	1—2
	51.4	1.778	<1
	53.0 — 53.2	1.728—1.722	2—3
	53.8 — 54.0	1.704—1.698	5—6
	54.3 — 54.4	1.689—1.687	2

## Example 51

Preparation of AlPO<sub>4</sub>-25

The crystalline metallophosphate denominated AlPO<sub>4</sub>-25 is preferably prepared by the thermally induced structural conversion of a less stable crystalline intermediate which is synthesized by hydrothermal crystallization from a reaction gel in a manner similar to that employed to obtain most of the AlPO<sub>4-n</sub> species of the present invention. This intermediate, identified as AlPO<sub>4</sub>-21 is readily synthesized using a considerable variety of organic templating agents which are removed from the structure during calcination to produce the stable AlPO<sub>4</sub>-25.

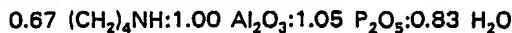
## O 043 562

(a) Preparation of AlPO<sub>4</sub>-21

A reaction mixture was prepared by combining 7.7 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 25.9 grams of water, to which was added 4.6 grams of a pseudo-boehmite phase (74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 2.4 grams of 5 (CH<sub>2</sub>)<sub>4</sub>:NH, (pyrrolidine), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 150°C at autogenous pressure for 150 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. Chemical analysis of 10 the product showed 10.2 wt.-% C, 3.2 wt.-% N, 32.1 wt. % Al<sub>2</sub>O<sub>3</sub>, 47.1 wt. % P<sub>2</sub>O<sub>5</sub>, 19.8 wt. % LOI, giving a product composition in molar oxide ratios of:



15 The product was designated AlPO<sub>4</sub>-21, and had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

	2θ	d	100×I/I <sub>0</sub>
20			
	10.0	8.845	51
	10.5	8.425	7
	11.3	7.830	14
	11.8	7.500	13
25	12.2	7.255	36
	13.2	6.707	6
	14.2	6.237	36
	14.6	6.067	27
	15.9	5.574	31
30	16.8	5.277	6
	18.5	4.796	4
	19.6	4.529	11
	20.4	4.353	25
	21.1	4.210	25
35	21.3	4.171	30
	22.6	3.934	97
	22.8	3.900	88
	23.7	3.754	23
	25.1	3.548	100
40	25.8	3.453	6
	26.2	3.401	19
	26.6	3.351	53
	27.6	3.232	47
	28.2	3.164	21
45	29.0	3.079	11
	29.4	3.038	3
	30.6	2.921	5
	31.0	2.885	8
	32.0	2.797	35
50	32.6	2.747	23
	32.9	2.722	38
	34.0	2.637	15
	35.2	2.550	2
	35.9	2.501	6
55	37.2	2.417	12
	37.8	2.380	3
	38.8	2.321	5
	40.2	2.243	7
	44.4	2.040	7
60	47.6	1.910	8
	50.8	1.797	7
	52.0	1.759	9
	52.6	1.740	11
	53.2	1.722	8
65	54.0	1.698	7

## O 043 562

(b) A procedure similar to that in part (a) above was followed except where indicated in Table E. A portion of the solid product from each reaction was subjected to X-ray analysis and in each case a phase characterized by an X-ray powder diffraction pattern essentially the same as that in part (a) was observed alone or in admixture.

5

**TABLE E**  
Reaction mixture composition

	Example #	Organic used (R)	R	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O	Digestion time (hrs)	Temp (°C)
10	(b) 1	(CH <sub>3</sub> ) <sub>3</sub> N trimethylamine	1	1	1	50	94	150
	(b) 2	(CH <sub>3</sub> ) <sub>2</sub> NH pyrrolidine	1	1	1	50	166	150
	(b) 3	C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> 1,4-dimethyl piperazine	1	1	1	50	168	200
15	(b) 4	C <sub>11</sub> H <sub>28</sub> N <sub>2</sub> 3-(di-n-butyl-amino)-propylamine	1	1	1	40	168	200
	(b) 5	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> N,N,N',N'-tetra-methyl-1,3-propane-diamine	1	1	1	40	168	200
20	(b) 6	C <sub>6</sub> H <sub>11</sub> NO N,N-dimethyl-ethanolamine	1	1	1	40	336	200
	(b) 7	n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> n-propylamine	1	1	1	50	334	200
25	(b) 8	C <sub>4</sub> H <sub>16</sub> N <sub>2</sub> N,N,N',N'-tetra-methyl-ethylene-diamine	1	1	1	50	168	200
	(b) 9	C <sub>3</sub> H <sub>8</sub> NO N-methyl-ethanolamine	1	1	1	50	168	200

### Preparation of AlPO<sub>4</sub>-25

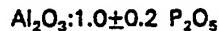
(c) A portion of the AlPO<sub>4</sub>-21 crystalline product obtained in part (a) was calcined in air at about 30 600°C for 2 hours. The calcined product had an X-ray powder diffraction pattern quite different from the starting AlPO<sub>4</sub>-21 and is a new and novel microporous aluminophosphate species denominated AlPO<sub>4</sub>-25. The X-ray pattern of this species is characterized by the following data:

	2θ	d	100xI/I <sub>0</sub>
35	7.6	11.632	3
	9.6	9.213	83
	10.6	8.346	1
	11.8	7.500	14
	12.6	7.025	3
	15.2	5.829	100
40	19.1	4.647	71
	21.3	4.171	84
	22.7	3.917	17
	23.6	3.770	8
	24.6	3.619	6
	25.5	3.490	43
45	26.1	3.414	14
	28.6	3.121	10
	29.9	2.988	3
	31.0	2.885	23
	33.2	2.698	8
	35.7	2.515	7
50	37.4	2.404	8
	37.9	2.374	8
	43.2	2.094	3
	53.3	1.719	3

(d) Five AlPO<sub>4</sub>-21 samples crystallized in parts (b)1, (b)3, (b)5, (b)7 and (b)9, respectively, were 60 calcined at 500—600°C in air and found to convert to the crystal structure characteristic of AlPO<sub>4</sub>-25. It is believed all AlPO<sub>4</sub>-21 compositions can be converted to AlPO<sub>4</sub>-25 in a similar manner.

The species AlPO<sub>4</sub>-25 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar oxides, is

65



## O 043 562

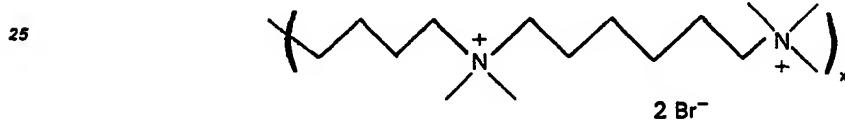
and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 23 below:

5	2θ	d	100xI/I <sub>0</sub>
10	9.4	9.41	32—96
	15.0	5.91	35—76
	18.8—18.9	4.72—4.70	35—100
	21.1	4.21	28—100
	22.5	3.95	16—32
	25.3	3.52	14—37
	30.8—30.9	2.90—2.89	20—31

15 Example 52

Preparation of AlPO<sub>4</sub>-26

A solution of 200 grams 1,4-dibromobutane in 500°cc of a 4:1 volume mixture of dimethylformamide:methanol (DMF/MeOH) was prepared and cooled to 0° in an ice/water bath. To this was added a solution of 159.4 grams N,N,N',N'-tetramethyl-1,6-hexanediamine in 500 cm<sup>3</sup> 4:1 DMF/MeOH. This mixture was stirred for three days, gradually warming to ambient temperature. The product mass was slurried in diethylether, filtered, washed with ether and dried in air at ambient temperature. The product was a polymeric quaternary ammonium salt, [(C<sub>14</sub>H<sub>32</sub>N<sub>2</sub>)Br<sub>2</sub>]<sub>x</sub>:



30 In order to obtain the hydroxide form, 200 grams of the above polymer was dissolved in 800 grams of H<sub>2</sub>O and added dropwise over 6 hours to a stirred suspension of 131.4 grams Ag<sub>2</sub>O in 1000 grams H<sub>2</sub>O. The resulting mixture was stirred overnight and filtered. Chemical analysis of the filtrate showed 1.9 wt. % C, 0.32 wt. % N, and 0.014 wt. % Br, corresponding to an aqueous solution containing 3.0 wt. % of the polymer [(C<sub>14</sub>H<sub>32</sub>N<sub>2</sub>)(OH)<sub>2</sub>]<sub>x</sub>. The concentration of the polymer in a portion of the filtrate was increased to 12.9 wt. % by removing H<sub>2</sub>O at reduced pressure.

35 A reaction mixture was prepared by combining 101.6 grams of the above aqueous solution containing 12.9 wt. % of the polymeric quaternary ammonium hydroxide with 6.9 grams of a hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O). This mixture was stirred until homogeneous. To this mixture was added 11.5 grams 85 wt. % orthophosphoric acid and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



45 The reaction mixture was placed in a sealed stainless steel pressure vessel having an inert liner and heated in an oven at 200°C at autogenous pressure for 24 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. The resulting AlPO<sub>4</sub>-26 product had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

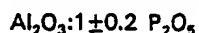
50	2θ	d	100xI/I <sub>0</sub>
55	8.35	10.59	100
	9.85	8.98	14
	10.2	8.67	(sh)
	10.55	8.38	68
	11.8	7.50	1
	13.5	6.56	8
	14.5	6.11	6
60	15.45	5.73	3
	16.8	5.28	10
	17.65	5.02	15
	18.05	4.91	18
	19.0	4.67	1

## 0 043 562

TABLE 24 (contd.)

	2θ	d	100xI/Io
5	19.9	4.46	11
	20.3	4.37	1
	21.65	4.10	4
	22.25	3.99	31
	23.05	3.86}	
	22.9	3.88}	74
10	24.7	3.60	6
	25.25	3.527	10
	25.85	3.446	2
	27.2	3.278	10
	27.45	3.249	6
15	27.95	3.192	6
	29.2	3.058	4
	29.7	3.008	1
	30.45	3.936	9
	30.9	2.8938}	
20	31.1	2.875	12
	31.6	2.83	2
	32.25	2.776	8
	32.7	2.739	1
	33.8	2.652	1
25	34.3	2.614	6
	35.0	2.564	1
	35.4	2.536	1
	36.15	2.485	<1
	36.4	2.468	<1
30	37.45	2.401	2
	38.6	2.332	<1
	39.0	2.309	<1
	39.4	2.287	1
	40.0	2.254	<1
35	40.5	2.227	2
	41.3	2.186	2
	42.4	2.132	2
	43.1	2.099	4
	44.2	2.049	<1
40	45.7	1.985	<1
	46.1	1.969	1
	47.8	1.903	1
	48.15	1.890	2
	49.1	1.855	2
45	49.7	1.834	<1
	50.7	1.801	<1
	51.4	1.778	2
	52.5	1.743	1
	52.9	1.731	<1
50	53.7	1.707	2
	54.4	1.687	3
	55.2	1.664	1

The species AlPO<sub>4</sub>-26 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides is:



and having an X-ray powder diffraction pattern essentially as set forth in Table 24.

60 Example 53

Preparation of AlPO<sub>4</sub>-28

The crystalline metallophosphate denominated AlPO<sub>4</sub>-28 is preferably prepared by the thermally induced structural conversion of a less stable crystalline intermediate which is synthesized by hydr thermal crystallizati n from a reaction gel in a manner similar to that employed to obtain most of

## O 043 562

the AlPO<sub>4</sub>-n species of the present invention. This intermediate, identified as AlPO<sub>4</sub>-23 is readily synthesized using pyrrolidine as the templating agent which is removed from the structure during calcination to produce the stable AlPO<sub>4</sub>-28.

**5 (a) Preparation of AlPO<sub>4</sub>-23**

A reaction mixture was prepared by combining 23.1 grams of 85% orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 77.6 grams of water, to which was added 13.8 grams of a hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O), and stirred until homogeneous. To this mixture was added 7.1 grams of (CH<sub>2</sub>)<sub>4</sub>:NH (pyrrolidine), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was placed in a sealed stainless steel pressure vessel lined with an inert plastic material and heated in an oven at 200°C at autogenous pressure for 91 hours. The solid reaction product was recovered by filtration, washed with water, and dried in air at 110°C. Chemical analysis showed 9.9 wt. % C, 31. wt. % N, 32.8 wt. % Al<sub>2</sub>O<sub>3</sub>, 47.5 wt. % P<sub>2</sub>O<sub>5</sub>, 19.3 wt. % LOI, giving a product composition in molar oxide ratios of:



The product denominated AlPO<sub>4</sub>-23 had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

25	2θ	d	100xI/I <sub>0</sub>
30	7.4	11.946	47
	10.3	8.588	24
	10.7	8.268	64
	11.6	7.628	54
	11.9	7.437	43 (sh)
	13.4	6.607	4
35	14.7	6.026	4
	15.0	5.906	6
	16.8	5.277	6
	19.0	4.671	21
	20.4	4.353	28
	21.3	4.171	100
40	23.2	3.834	65
	24.0	3.708	9
	24.5	3.633	6 (sh)
	26.2	3.401	16
	27.2	3.278	11
	27.8	3.209	12
45	28.6	3.121	36
	29.6	3.018	30
	30.8	2.903	11
	32.2	2.780	74
	33.8	2.652	2
	34.9	2.571	7
50	36.2	2.481	8
	37.4	2.404	4
	39.2	2.298	2
	40.7	2.217	7
	43.3	2.090	4
	48.2	1.888	8
55	49.8	1.831	4
	51.8	1.765	2
	52.8	1.734	5

**(b) Preparation of AlPO<sub>4</sub>-28**

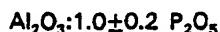
A portion of the AlPO<sub>4</sub>-23 composition prepared in part (a), supra, was calcined in air at about 600°C for 2 hours. The calcined product was crystalline but had an X-ray powder diffraction pattern substantially different from the precursor material. It is apparent that the calcination procedure

## 0 043 562

converted the original AlPO<sub>4</sub>-23 to a new microporous aluminophosphate species of the present invention, namely AlPO<sub>4</sub>-28. The X-ray powder diffraction pattern of the AlPO<sub>4</sub>-28 product is as follows:

	2θ	d	100xI/I <sub>0</sub>
10	7.9	11.191	41
	9.9	8.934	7
	12.2	7.255	100
	13.3 (sh)	6.657	22
	15.7	5.644	7
	18.6	4.770	47
	19.2 (sh)	4.623	25
	21.0	4.230	9
	21.9	4.058	30
	~23.5	3.786	7
20	25.4	3.507	20
	26.1	3.414	13
	27.0	3.302	16
	29.7	3.008	13
	30.9	2.894	13
	32.1	2.788	11
	35.4	2.536	6
	36.4	2.468	2

The species AlPO<sub>4</sub>-28 as herein referred to is a crystalline metallophosphate whose essential framework structure has a chemical composition, expressed in terms of molar ratios of oxides, is



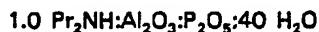
and having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 25 below:

	2θ	d	100xI/I <sub>0</sub>
40	7.9	11.19	41
	12.2	7.26	100
	18.6	4.77	47
	21.9	4.06	30
	25.4	3.51	20
	27.0	3.30	16

### Example 54

#### Preparation of AlPO<sub>4</sub>-31

(a) A reaction mixture was prepared by dispersing 164.8 grams of a pseudo-boehmite phase (74.2 wt. % Al<sub>2</sub>O<sub>3</sub>, 25.8 wt. % H<sub>2</sub>O) in 715.2 grams of water, to which was added 276.7 grams of 85% orthophosphoric acid, and stirred until homogeneous. To this mixture was added 121.4 grams of di-(n-propyl)amine (Pr<sub>2</sub>NH), and the mixture stirred until homogeneous. The composition of the final reaction mixture in molar oxide ratios was:



The reaction mixture was sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 200°C at autogeneous pressure for 46 hours. The solid reaction product was recovered by repeated centrifugation and washing with H<sub>2</sub>O, and dried in air at room temperature. Chemical analysis of the reaction product showed 4.7 wt. % C, 0.85 wt. % N, 37.4 wt. % Al<sub>2</sub>O<sub>3</sub>, 51.6 wt. % P<sub>2</sub>O<sub>5</sub>, 10.3 wt. % LOI, giving a product composition expressed in molar oxide ratios of



The above product, denominated AlPO<sub>4</sub>-31, had an X-ray powder diffraction pattern characterized by the following data, wherein "I" is the intensity and "d" the interplanar spacing:

## O 043 562

TABLE 26

	$2\theta$	d	$100 \times I/I_0$
5	8.5	10.40	85
	9.5	9.31	12
	13.35	6.63	6
	13.8	6.42	2
	14.8	5.99	2
10	15.7	5.64	6
	17.1	5.19	7
	18.3	4.85	7
	20.0 (sh)	4.44	—
	20.3	4.37	48
15	21.1	4.21	28
	21.8	4.08	26
	22.6	3.93	100
	23.2 (sh)	3.83	—
	24.8	3.59	7
20	25.6	3.48	8
	27.7	3.22	11
	28.3	3.15	7
	29.6	3.02	9
	29.9	2.99	9
25	31.4 (sh)	2.85	—
	31.6	2.83	14
	35.2	2.55	10
	35.8	2.51	6
	38.0	2.37	8
30	40.0	2.25	4

(b) A portion of the solid crystalline product obtained above was calcined to a temperature of 1000°C. This calcined material had an X-ray powder diffraction pattern essentially identical to that of part (a).

## 35 Example 55

(a) Adsorption capacities of AlPO<sub>4</sub>-5 (prepared in Ex. 3(b) supra) were measured using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
O <sub>2</sub>	0.346	129	-183	12.6
O <sub>2</sub>	0.346	999	-183	17.0
45 Neopentane	0.62	136	24	5.5
(C <sub>4</sub> F <sub>9</sub> ) <sub>3</sub> N (after 4 hours)	1.0	0.097	24	1.2
H <sub>2</sub> O	0.265	6.13	24	4.6
H <sub>2</sub> O	0.265	24.6	23	26.4

50 The pore size of the calcined product is greater than 0.6 and less than 1.0 nm as shown by adsorption of neopentane, kinetic diameter of 0.62 nm, and nil adsorption of (C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>N, kinetic diameter of 1.0 nm.

(b) Adsorption capacities of AlPO<sub>4</sub>-5 (prepared in Example 2(b) supra) were measured using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
60 O <sub>2</sub>	0.346	132	-183	13.3
O <sub>2</sub>	0.346	973	-183	18.3
Cyclohexane	0.60	72	24	9.5
Neopentane	0.62	136	24	4.8
H <sub>2</sub> O	0.265	6.1	24	3.9
65 H <sub>2</sub> O	0.265	28	24	29.8

## O 043 562

The pore size of the calcined product is greater than 0.62 nm, as shown by adsorption of neopentane, kinetic diameter of 0.62 nm.

(c) Adsorption capacities of AlPO<sub>4</sub>-5 (prepared in a manner similar to that of Example 2(b) supra) were measured using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
10 O <sub>2</sub>	0.346	140	-183	14.6
O <sub>2</sub>	0.346	940	-183	21.3
Neopentane	0.62	137	25	6.5
H <sub>2</sub> O	0.265	6.1	25	6.5
H <sub>2</sub> O	0.265	27.6	25	32.6

### Example 56

Adsorption capacities of AlPO<sub>4</sub>-28 (prepared in Example 53(b), supra) were measured using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
25 O <sub>2</sub>	0.346	137	-183	1.0
O <sub>2</sub>	0.346	1014	-183	2.5
n-Hexane	0.43	37	24	0.4
Neopentane	0.62	413	24	0.5
H <sub>2</sub> O	0.265	6.1	24	11.1
H <sub>2</sub> O	0.265	26.7	24	21.4

30 The pore size of the calcined product is >0.265 nm and <0.346 nm as shown by adsorption of H<sub>2</sub>O, kinetic diameter of 0.265 nm, and nil adsorption of O<sub>2</sub>, kinetic diameter of 0.346 nm.

### Example 57

35 Adsorption capacities of AlPO<sub>4</sub>-25 (prepared in Ex. 52(c), supra) were measured using a standard McBain Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
40 O <sub>2</sub>	0.346	137	-183	4.9
O <sub>2</sub>	0.346	1014	-183	5.9
n-Hexane	0.43	37.3	25	0.3
45 Neopentane	0.62	413	25	0.4
H <sub>2</sub> O	0.265	6.1	25	4.4
H <sub>2</sub> O	0.265	26.7	25	16.6

50 The pore size of the calcined product is >0.34 nm and <0.43 nm as shown by adsorption of O<sub>2</sub>, kinetic diameter of 0.346 nm, and nil adsorption of n-hexane, kinetic diameter of 0.43 nm.

### Example 58

55 Adsorption capacities of AlPO<sub>4</sub>-20 (prepared as in Example 47(b) supra) were measured using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
60 O <sub>2</sub>	0.346	129	-183	2.7
O <sub>2</sub>	0.346	1000	-183	11.5
n-Hexane	0.43	60	24	1.7
Ne pentane	0.62	404	24	1.5
Cyclohexane	0.60	14.7	24	1.3
H <sub>2</sub> O	0.265	6.1	24	22.6
65 H <sub>2</sub> O	0.265	24.7	24	37.2

## O 043 562

The pore size of the calcined product is ca. 0.3 nm, as shown by adsorption of H<sub>2</sub>O, kinetic diameter of 0.265 nm, and low adsorption at low partial pressure of O<sub>2</sub>, kinetic diameter of 0.346 nm.

### Example 59

5 Adsorption capacities of AlPO<sub>4</sub>-17 (prepared in Ex. 42(c) supra) using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
10 O <sub>2</sub>	0.346	136	-183	22.2
O <sub>2</sub>	0.346	965	-183	23.1
n-Hexane	0.43	60	23	7.7
Isobutane	0.50	135	22	0.2
15 Neopentane	0.62	410	23	0.3
H <sub>2</sub> O	0.265	6.1	22	24.9
H <sub>2</sub> O	0.265	24	22	27.8

20 The pore size of the calcined product is 0.43 nm and 0.5 nm, as shown by adsorption of n-hexane, kinetic diameter of 0.43 nm, and nil adsorption of isobutane, kinetic diameter of 0.5 nm.

### Example 60

25 Adsorption capacities of AlPO<sub>4</sub>-16 (prepared in Example 41(d) supra) were measured using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
30 O <sub>2</sub>	0.346	135	-183	1.2
O <sub>2</sub>	0.346	1006	-183	11.6
n-Butane	0.43	1024	24	2.0
Neopentane	0.62	401	25	1.4
35 H <sub>2</sub> O	0.265	6.1	24	19.0
H <sub>2</sub> O	0.265	26.7	24	36.3

40 The pore size of the calcined product is >0.265 nm and <0.346 nm, as shown by adsorption of H<sub>2</sub>O, kinetic diameter of 0.265 nm, and low adsorption of O<sub>2</sub> at low partial pressures kinetic diameter of 0.346 nm.

### Example 61

45 Adsorption capacities of AlPO<sub>4</sub>-14 (prepared in Ex. 39(b) supra) using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C.

Adsorbate	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
50 O <sub>2</sub>	0.346	136	-183	15.53
O <sub>2</sub>	0.346	1017	-183	21.56
n-Hexane	0.43	60	26	0.25
Neopentane	0.62	655	24	0.37
H <sub>2</sub> O	0.265	6.1	24	21.46
55 H <sub>2</sub> O	0.265	28	24	28.66
N <sub>2</sub>	0.364	133	-196	11.28
N <sub>2</sub>	0.364	996	-196	14.99

60 The pore size of the calcined product is >0.364 nm and <0.43 nm as shown by adsorption of N<sub>2</sub>, kinetic diameter of 0.364 nm, and nil adsorption of n-hexane, kinetic diameter of 0.43 nm.

### Example 62-A

65 Adsorption capacities of AlPO<sub>4</sub>-8 (prepared as in Example 29, supra) using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

**O 043 562**

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt % adsorbed
5 O <sub>2</sub>	0.346	135	-183	8.9
5 O <sub>2</sub>	0.346	1006	-183	18.6
n-Butane	0.43	1024	24	5.0
Neopentane	0.62	668	24	4.5
(C <sub>4</sub> F <sub>9</sub> ) <sub>3</sub> N (after 4 hours)	0.10	0.1	25	8.2
H <sub>2</sub> O	0.265	61	24	18.5
10 H <sub>2</sub> O	0.265	267	24	31.9

The pore size of the calcined product is greater than 0.62 nm as shown by adsorption of neopentane, kinetic diameter of 0.62 nm.

**15 Example 62-B**

Adsorption capacities of AlPO<sub>4</sub>-31 (prepared as in Example 54(b) supra except that product was calcined to a temperature of 600°C) were measured using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt % adsorbed
20 O <sub>2</sub>	0.346	132	-183	8.1
20 O <sub>2</sub>	0.346	948	-183	11.5
25 Butane	0.43	143	24	4.0
Cyclohexane	0.60	72	24	5.3
Neopentane	0.62	145	24	3.1
H <sub>2</sub> O	0.265	6.1	24	5.3
H <sub>2</sub> O	0.265	18.7	24	13.9

30 The pore size is larger than 0.62 nm as shown by the adsorption of neopentane.

**Example 63**

A portion of the crystalline AlPO<sub>4</sub>-11 product of Example 32(a) supra was calcined in air from 35 200°C to 500°C over a period of 1 hour, followed by heating at 500°C for 2 hours.

Adsorption capacities were measured on this calcined product using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C.

	Kinetic diameter, nm	Pressure mbar	Temp., °C	Wt % adsorbed
40 Adsorbate				
40 O <sub>2</sub>	0.346	135	-183	9.22
40 O <sub>2</sub>	0.346	1006	-183	10.7
45 N-butane	0.43	405	24	4.35
45 Isobutane	0.50	669	24	4.71
Neopentane	0.62	401	24	1.22
Cyclohexane	0.60	40	24	5.30
H <sub>2</sub> O	0.265	6.1	24	11.8
H <sub>2</sub> O	0.265	26.7	24	16.4

50 The pore size of the calcined product is greater than 0.6 nm and less than 0.62 nm, as shown by adsorption of cyclohexane, kinetic diameter of 0.6 nm and nil adsorption of neopentane, kinetic diameter of 0.62 nm.

**55 Example 64**

Adsorption capacities of AlPO<sub>4</sub>-18 (prepared in Example 46(b) supra) were measured using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at 350°C:

60

65

**O 043 562**

	Kinetic diameter, nm	Pressure, mbar	Temp., °C	Wt. % adsorbed
O <sub>2</sub>	0.346	173	-183	23.0
O <sub>2</sub>	0.346	929	-183	27.9
n-Butane	0.43	957	24	16.2
iso-Butane	0.50	135	24	0.1
H <sub>2</sub> O	0.265	6.1	24	30.3
H <sub>2</sub> O	0.265	28	24	36.9

10 The pore size of the calcined product is 0.43 and 0.5 nm, as shown by adsorption of n-butane and nil adsorption of iso-butane at low partial pressure.

15 Somewhat surprisingly the aluminophosphate compositions of the present invention are found to be strongly hydrophilic. All species are observed to adsorb water preferentially over common hydrocarbon molecules such as paraffins, olefins and benzenoid aromatic species, e.g., benzene, xylenes and cumene. Thus the present aluminophosphates as a class are useful as desiccants in such adsorption separation/purification processes as natural gas drying, cracked gas drying. Water is also preferentially adsorbed over the so-called permanent gases such as carbon dioxide, nitrogen, oxygen and hydrogen. These aluminophosphates are therefore suitably employed in the drying of reformer 20 hydrogen streams and in the drying of oxygen, nitrogen or air prior to liquefaction. In this respect the adsorptive properties of the present aluminophosphates appears to be quite similar to those of the low silica aluminosilicate zeolites, despite the fact that they exhibit essentially no ion-exchange capacity—a quintessential property of zeolites.

25 The adsorptive properties of the present AlPO<sub>4</sub>-n compositions are illustrated by the data set forth in Table F and Table G below.

TABLE F  
Static drying of moist air at room temperature  
% Humidity

30	Sample	Initial	Final	Contact time, hours
				3
	Zeolite 4A	60	21	
35	Zeolite 5A	54	5	16
	Silica gel	56	18	16
	AlPO <sub>4</sub> -5	55	29	4
	AlPO <sub>4</sub> -8	60	21	3.5
40	AlPO <sub>4</sub> -8	61	19	18
	AlPO <sub>4</sub> -11	57	29	5.5
	AlPO <sub>4</sub> -14	56	19	3.0
	AlPO <sub>4</sub> -16	70	22	3.0
	AlPO <sub>4</sub> -16	56	14	72
45	AlPO <sub>4</sub> -17	63	24	18.5
	AlPO <sub>4</sub> -20	60	17	16
	AlPO <sub>4</sub> -28	56	7	17.5
	AlPO <sub>4</sub> -25	56	25	18.5
	AlPO <sub>4</sub> -9	51	29	23
50	AlPO <sub>4</sub> -18	56	19	24
	AlPO <sub>4</sub> -31	51	24	19

To illustrate the hydrophilic character of the AlPO<sub>4</sub>-n compositions in contact with an aqueous organic solution, dehydrated samples of AlPO<sub>4</sub> compounds and prior known comparison adsorbent, each weighing 0.5 grams were placed in 2 grams of a solution of 4 vol.-% H<sub>2</sub>O and 96 vol.-% 2-  
55 butanone at ambient room temperature and agitated moderately for 2 hours. Thereafter the residual solution and the adsorbent were analyzed for water content. The results appear below:

60

65

## O 043 562

TABLE G  
% Water removal  
from solution

	Adsorbent	% Loading**
5	AlPO <sub>4</sub> -5	55
	AlPO <sub>4</sub> -8	74
	AlPO <sub>4</sub> -11	21
	AlPO <sub>4</sub> -14	>80
	AlPO <sub>4</sub> -16	>80
10	AlPO <sub>4</sub> -17	77
	AlPO <sub>4</sub> -20	87
	Zeolite NaY	80
	Silica gel	28
15	Silicalite*	-5

\* U.S.—A—4,061,724

\*\* Percent of maximum theoretical capacity.

The present AlPO<sub>4</sub>-n compositions exhibit novel surface selectivity characteristics which render them useful as catalyst or catalyst bases in a number of hydrocarbon conversion and oxidative combustion reactions. They can be impregnated or otherwise loaded with catalytically active metals by methods well known in the art and used, for example, in fabricating catalysts compositions having silicalite or alumina bases. Of the general class, those species having pores larger than about 5Å are preferred.

Among the hydrocarbon conversion reactions catalyzed by AlPO<sub>4</sub>-n compositions are cracking, hydrocracking, alkylation of both the aromatic and isoparaffin types, isomerization including xylene isomerization, polymerization, reforming, hydrogenation, dehydrogenation, transalkylation, dealkylation and hydration.

Using AlPO<sub>4</sub>-n catalysts compositions which contain a hydrogenation promoter such as platinum or palladium, heavy petroleum residual stocks, cyclic stocks and other hydrocrackable charge stocks can be hydrocracked at temperatures in the range of 204°C to 441°C using molar ratios of hydrogen to hydrocarbon in the range of between 2 and 80, pressures between 1.67 and 242 bar, and a liquid hourly space velocity (LHSV) of from 0.1 to 20, preferably 1.0 to 10.

The AlPO<sub>4</sub>-n catalyst compositions employed in hydrocracking are also suitable for use in reforming processes in which the hydrocarbon feedstocks contact the catalyst at temperatures of from about 371°C to 538°C, hydrogen pressures of from 7.9 to 35.4 bar, LHSV values in the range of 0.1 to 10 and hydrogen to hydrocarbon molar ratios in the range of 1 to 20, preferably between 4 and 12.

These same catalysts, i.e. those containing hydrogenation promoters, are also useful in hydroisomerization processes in which feedstocks such as normal paraffins are converted to saturated branched chain isomers. Hydroisomerization is carried out at a temperature of from about 93°C to 316°C preferably 149°C to 287°C with an LHSV value of from about 0.2 to 1.0. Hydrogen is supplied to the reactor in admixture with the hydrocarbon feedstock in molar proportions (H/Hc) of between 1 and 5.

At somewhat higher temperatures, i.e. from about 344°C to 538°C, preferably 455°C to 510°C and usually at somewhat lower pressures within the range of about 2.0 to 4.43 bar, the same catalyst compositions are used to hydroisomerize normal paraffins. Preferably the paraffin feedstock comprises normal paraffins having a carbon number range of C<sub>7</sub>—C<sub>20</sub>. Contact time between the feedstock and the catalyst is generally relatively short to avoid undesirable side reactions such as olefin polymerization and paraffin cracking. LHSV values in the range of 0.1 to 10, preferably 1.0 to 6.0 are suitable.

The unique crystal structure of the present AlPO<sub>4</sub> catalysts and their total lack of alkali metal content favor their use in the conversion of alkylaromatic compounds, particularly the catalytic disproportionation of toluene, ethylene, trimethyl benzenes, tetramethyl benzenes and the like. In the disproportionation process isomerization and transalkylation can also occur. Group VIII noble metal adjuvents alone or in conjunction with Group VI—B metals such as tungsten, molybdenum and chromium are preferably included in the catalyst composition in amounts of from about 3 to 15 weight-% of the overall composition. Extraneous hydrogen can, but need not be present in the reaction zone which is maintained at a temperature of from about 204°C to 399°C pressures in the range of 7.9 to 139 bar and LHSV values in the range of 0.1 to 15.

Catalytic cracking processes are preferably carried out with AlPO<sub>4</sub>-n compositions using feedstocks such as gas oils, heavy naphthas, deasphalted crude oil residua etc. with gasoline being the principal desired product. Temperature conditions of 455°C to 593°C, LHSV values of 0.5 to 10 and pressure conditions of from about 0.98 to 4.43 bar are suitable.

Dehydrocyclization reactions employing paraffinic hydrocarbon feedstocks, preferably normal paraffins having more than 6 carbon atoms, to form benzene, xylenes, toluene and the like are carried out using essentially the same reaction conditions as for catalytic cracking. For these reactions it is

## O 043 562

preferred to use the AlPO<sub>4</sub>-n catalyst in conjunction with a Group VIII non-noble metal cation such as cobalt and nickel.

In catalytic dealkylation wherein it is desired to cleave paraffinic side chains from aromatic nuclei without substantially hydrogenating the ring structure, relatively high temperatures in the range of about 427°C—538°C are employed at moderate hydrogen pressures of about 21.7—69.9 bar, other conditions being similar to those described above for catalytic hydrocracking. Preferred catalysts are of the same type described above in connection with catalytic dehydrocyclization. Particularly desirable dealkylation reactions contemplated herein include the conversion of methylnaphthalene to naphthalene and toluene and/or xylenes to benzene.

In catalytic hydrofining, the primary objective is to promote the selective hydrodecomposition of organic sulfur and/or nitrogen compounds in the feed, without substantially affecting hydrocarbon molecules therein. For this purpose it is preferred to employ the same general conditions described above for catalytic hydrocracking, and catalysts of the same general nature described in connection with dehydrocyclization operations. Feedstocks include gasoline fractions, kerosenes, jet fuel fractions, diesel fractions, light and heavy gas oils, deasphalted crude oil residua and the like any of which may contain up to about 5 weight-percent of sulfur and up to about 3 weight-percent of nitrogen.

Similar conditions can be employed to effect hydrofining, i.e., denitrogenation and desulfurization, of hydrocarbon feeds containing substantial proportions of organonitrogen and organosulfur compounds. It is generally recognized that the presence of substantial amounts of such constituents markedly inhibits the activity of catalysts for hydrocracking. Consequently, it is necessary to operate at more extreme conditions when it is desired to obtain the same degree of hydrocracking conversion per pass on a relatively nitrogenous feed than are required with a feed containing less organonitrogen compounds. Consequently, the conditions under which denitrogenation, desulfurization and/or hydrocracking can be most expeditiously accomplished in any given situation are necessarily determined in view of the characteristics of the feedstocks in particular the concentration of organonitrogen compounds in the feedstock. As a result of the effect of organonitrogen compounds on the hydrocracking activity of these compositions it is not at all unlikely that the conditions most suitable for denitrogenation of a given feedstock having a relatively high organonitrogen content with minimal hydrocracking, e.g., less than 20 volume percent of fresh feed per pass, might be the same as those preferred for hydrocracking another feedstock having a lower concentration of hydrocracking inhibiting constituents e.g., organonitrogen compounds. Consequently, it has become the practice in this art to establish the conditions under which a certain feed is to be contacted on the basis of preliminary screening tests with the specific catalyst and feedstock.

Isomerization reactions are carried out under conditions similar to those described above for reforming, using somewhat more acidic catalysts. Olefins are preferably isomerized at temperatures of 260°—482°C, while paraffins, naphthenes and alkyl aromatics are isomerized at temperatures of 371°—538°C. Particularly desirable isomerization reactions contemplated herein include the conversion of n-heptane and/or n-octane to isoheptanes, iso-octanes, butane to iso-butane, methylcyclopentane to cyclohexane, meta-xylene and/or ortho-xylene to paraxylene, 1-butene to 2-butene and/or isobutene, n-hexene to isohexene, cyclohexene to methylcyclopentene etc. The preferred cation form is a combination of the AlPO<sub>4</sub>-n with polyvalent metal compounds (such as sulfides) of metals of Group II-A, Group II-B and rare earth metals. For alkylation and dealkylation processes the AlPO<sub>4</sub>-n compositions having pores of at least 0.5 nm are preferred. When employed for dealkylation of alkyl aromatics, the temperature is usually at least 177°C and ranges up to a temperature at which substantial cracking of the feedstock or conversion products occurs, generally up to about 371°C. The temperature is preferably at least 232°C and not greater than the critical temperature of the compound undergoing dealkylation. Pressure conditions are applied to retain at least the aromatic feed in the liquid state. For alkylation the temperature can be as low as 121°C but is preferably at least 177°C. In alkylation benzene, toluene and xylene, the preferred alkylating agent are olefins such as ethylene and propylene.

### Claims

1. Crystalline aluminophosphates each having a framework structure whose chemical composition expressed in terms of mole ratios of oxides is



characterized in that each of said framework structures being microporous in which the pores are uniform and have nominal diameters within the range of 0.3 to 1.0 nm, an intracrystalline adsorption capacity for water at 6.13 mbar and 24°C of at least 3.5 weight percent, the adsorption and desorption of water being completely reversible while retaining the same essential framework topology in both the hydrated and dehydrated state.

2. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 2.

**O 043 562**

3. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 4.
4. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 6.
5. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 8.
6. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 10.
7. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 12.
8. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 13.
9. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 15.
10. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 17.
11. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 19.
12. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 21.
13. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 23.
14. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern essentially as set forth in Table 24.
15. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table 25.
16. Crystalline aluminophosphate according to claim 1 which has an X-ray powder diffraction pattern essentially as set forth in Table 26.
17. Process for preparing a microporous crystalline aluminophosphate having a chemical composition expressed in terms of mole ratios of oxides of



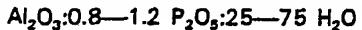
characterized by forming a reaction mixture having a composition expressed in terms of mole ratios of oxides of



and containing from about 0.2 to 2.0 moles of an organic templating agent per mole of  $\text{Al}_2\text{O}_3$ , and heating said reaction mixture at a temperature of at least 100°C until crystals of said aluminophosphate are produced.

18. Process according to claim 17 wherein the reaction mixture is heated at a temperature of from 100°C to 300°C under autogeneous pressure.

19. Process according to claim 18 wherein the reaction mixture has a composition expressed in terms of mole ratios of oxides of



and is heated at a temperature of from 125°C to 200°C.

20. Process according to claim 19 wherein the source of  $\text{P}_2\text{O}_5$  is phosphoric acid, the source of  $\text{Al}_2\text{O}_3$  is pseudo-boehmite hydrated aluminum oxide and the reaction mixture contains per mole of  $\text{Al}_2\text{O}_3$ , from 0.5 to 1.5 moles of organic templating agent, from 40 to 50 moles  $\text{H}_2\text{O}$  and about 1.0 mole  $\text{P}_2\text{O}_5$ .

21. Process according to claim 19 wherein the templating agent is selected from the group consisting of tetrapropylammonium hydroxide; tetraethylammonium hydroxide; tripropylamine; triethylamine; triethanolamine; piperidine; cyclohexylamine; 2-methyl pyridine; N,N-dimethylbenzylamine; N,N-diethylethanolamine; dicyclohexylamine; N,N-dimethylethanolamine; choline; N,N-dimethylpiperazine; 1,4-diazabicyclo(2.2.2)octane; N-methylethanolamine; N-methylethanolamine; N-methylpiperidine; 3-methylpiperidine; N-methylcyclohexylamine; 3-methylpyridine; 4-methylpyridine; quinuclidine; and N,N'-dimethyl-1,4-diazabicyclo(2.2.2)octane dihydroxide.

22. Process according to claim 19 wherein the templating agent is selected from the group consisting of tetramethylammonium hydroxide; tetraethylammonium hydroxide; tetrabutylammonium hydroxide; tetrapentylammonium hydroxide; di-(n-butyl)-amine; neopentylamine; di-(n-pentyl)-amine; isopropylamine and t-butylamine.

23. Process according to claim 19 wherein the templating agent is an alkyl amine in which the alkyl moiety contains from 2 to 7 carbon atoms.

## 0 043 562

24. Process according to claim 19 wherein the templating agent is selected from the group consisting of ethylenediamine and 2-imidazolidone.

25. Process according to claim 23 wherein the alkylamine is di-(n-propyl) amine.

26. Process according to claims 19 wherein the templating agent is a polymeric quaternary ammonium salt  $\{[C_{14}H_{32}N_2(OH)_2]_x\}$ , wherein X is a value of at least 2.

27. Process for separating polar molecular species having effective molecular diameter of less than about 1.0 nm from admixture with less polar molecular species by contacting said mixture with at least one aluminophosphate of claim 1, said aluminophosphate being at least partially dehydrated at the initiation of contact and have a pore diameter large enough to adsorb the more polar molecular species.

28. Process according to claim 27 wherein the more polar molecular species is water.

29. Process for converting a hydrocarbon which comprises contacting said hydrocarbon under hydrocarbon converting conditions with an aluminophosphate of claim 1.

30. Process according to claim 29 wherein the hydrocarbon conversion process is cracking.

31. Process according to claim 29 wherein the hydrocarbon conversion process is hydrocracking.

32. Process according to claim 29 wherein the hydrocarbon conversion process is hydrogenation.

33. Process according to claim 29 wherein the hydrocarbon conversion process is polymerization.

34. Process according to claim 29 wherein the hydrocarbon conversion process is alkylation.

35. Process according to claim 29 wherein the hydrocarbon conversion process is reforming.

36. Process according to claim 29 wherein the hydrocarbon conversion process is hydrotreating.

37. Process according to claim 29 wherein the hydrocarbon conversion process is isomerization.

38. Process according to claim 37 wherein the isomerization is xylene isomerization.

### Patentansprüche

25 1. Kristalline Aluminophosphate mit Gitterstruktur und der als Molverhältnis der Oxide ausgedrückten Zusammensetzung



30 dadurch gekennzeichnet, daß jede der Gitterstrukturen mikroporös ist, wobei die Poren gleichmäßig sind und Nenndurchmesser im Bereich von 0,3 bis 1 nm, eine interkristalline Adsorptionskapazität für Wasser bei 6,13 mbar und 24°C von wenigstens 3,5% haben und die Wasseraufnahme und -desorption vollständig reversibel ist und im wesentlichen die gleiche Gitterstruktur-Topologie sowohl im hydratisierten als auch im dehydratisierten Zustand beibehalten wird.

35 2. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, das wenigstens die d-Abstände gemäß der Tabelle 2 besitzt.

3. Kristallines Aluminophosphat gemäß Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, das wenigstens die in der Tabelle 4 wiedergegebenen d-Abstände besitzt.

40 4. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, das wenigstens die in Tabelle 6 wiedergegebenen d-Abstände besitzt.

5. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 8 wiedergegebenen d-Abstände aufweist.

45 6. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 10 wiedergegebenen d-Abstände aufweist.

7. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 12 wiedergegebenen d-Abstände aufweist.

50 8. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 13 wiedergegebenen d-Abstände aufweist.

9. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 15 wiedergegebenen d-Abstände aufweist.

55 10. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 17 wiedergegebenen d-Abstände aufweist.

11. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 19 wiedergegebenen d-Abstände aufweist.

60 12. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 21 wiedergegebenen d-Abstände aufweist.

13. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 23 wiedergegebenen d-Abstände aufweist.

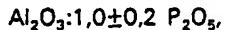
65 14. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 24 wiedergegebenen d-Abstände aufweist.

15. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 25 wiedergegebenen d-Abstände aufweist.

16. Kristallines Aluminophosphat nach Anspruch 1, das ein Röntgen-Pulverbeugungsbild hat, welches wenigstens die in Tabelle 26 wiedergegebenen d-Abstände aufweist.

## O 043 562

17. Verfahren zur Herstellung eines mikroporösen kristallinen Aluminophosphats der im Molverhältnis der Oxide ausgedrückten Zusammensetzung



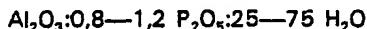
5 dadurch gekennzeichnet, daß man ein Reaktionsgemisch bildet, das eine im Molverhältnis der Oxide ausgedrückte Zusammensetzung von



10 hat und etwa 0,2 bis 2,0 Mol eines organischen strukturgebenden Mittels pro Mol  $\text{Al}_2\text{O}_3$  enthält, und das Reaktionsgemisch auf eine Temperatur von wenigstens 100°C bis zur Bildung von Kristallen des genannten Aluminophosphats, erhitzt.

18. Verfahren nach Anspruch 17, wobei das Reaktionsgemisch auf eine Temperatur von 100 bis 15 300°C unter Eigendruck erhitzt wird.

19. Verfahren nach Anspruch 18, wobei das Reaktionsgemisch eine im Molverhältnis der Oxide ausgedrückte Zusammensetzung von



20 besitzt und auf eine Temperatur von 125 bis 200°C erhitzt wird.

20. Verfahren nach Anspruch 19, wobei die Quelle für das  $\text{P}_2\text{O}_5$  Phosphorsäure, die Quelle für  $\text{Al}_2\text{O}_3$  hydratisiertes Aluminiumoxid, genannt Pseudoboehmit, ist und das Reaktionsgemisch pro Mol  $\text{Al}_2\text{O}_3$  0,5 bis 1,5 Mol des organischen Strukturbildners, 40 bis 50 Mol  $\text{H}_2\text{O}$  und etwa 1 Mol  $\text{P}_2\text{O}_5$  25 enthält.

21. Verfahren nach Anspruch 19, wobei der Strukturbildner aus der Gruppe der folgenden Verbindungen gewählt ist: Tetrapropylammoniumhydroxid; Tetraäthylammoniumhydroxid; Tripropylamin; Triäthylamin; Triäthanolamin; Pyridin; Cyclohexylamin; 2-Methylpyridin; N,N-Dimethylbenzylamin; N,N-Diäthyläthanolamin; Dicyclohexylamin; N,N-Dimethyläthanolamin; Cholin; N,N-Dimethylpiperazin; 1,4-Diazabicyclo-(2,2,2)-octan; N-Methyldiäthanolamin; N-Methyläthanolamin; N-Methylpiperidin; 3-Methylpiperidin; N-Methylcyclohexylamin; 3-Methylpyridin; 4-Methylpyridin; Quinuclidin; und N,N'-Dimethyl-1,4-diazabicyclo-(2,2,2)-octan-dihydroxid.

22. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Strukturbildner aus der folgenden Gruppe gewählt ist; Tetramethylammoniumhydroxid; Tetraäthylammoniumhydroxid; Tetra-35 butylammoniumhydroxid; Tetrapentylammoniumhydroxid; Di-(n-butyl)-amin; Neopentylamin; Di-(n-pentyl)amin; Isopropylamin und Tertiobutylamin.

23. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Strukturbildner ein Alkylamin ist, in dem die Alkylkette 2 bis 7 Kohlenstoffatome enthält.

24. Verfahren nach Anspruch 19, wobei der Strukturbildner aus der Gruppe von Äthylendiamin 40 und 2-Imidazolidon gewählt ist.

25. Verfahren nach Anspruch 23, wobei das Alkylamin Di-(n-propyl)amin ist.

26. Verfahren nach Anspruch 19, wobei der Strukturbildner ein polymeres quaternäres Ammoniumsalz  $[(\text{C}_{14}\text{H}_{32}\text{N}_2)(\text{OH})_2]_x$  ist, in dem X wenigstens den Wert 2 hat.

27. Verfahren zur Abtrennung von polaren Molekülarten mit einem effektiven Moleküldurchmesser von weniger als etwa 1,0 nm aus einem Gemisch mit weniger polaren Molekülarten durch Inberührungsbringen dieses Gemisches mit wenigstens einem Aluminophosphat nach Anspruch 1, wobei das genannte Aluminophosphat bei Kontaktbeginn wenigstens teilweise dehydratisiert ist und einen genügend großen Porendurchmesser hat, um die stärker polare Molekülart zu adsorbieren.

28. Verfahren nach Anspruch 27, wobei die stärker polare Molekülart Wasser ist.

29. Verfahren zum Umwandlung eines Kohlenwasserstoffes, bei dem der Kohlenwasserstoff unter Kohlenwasserstoffumwandlungsbedingungen mit einem Aluminophosphat nach Anspruch 1 in Berührung gebracht wird.

30. Verfahren nach Anspruch 29, worin der Kohlenwasserstoffumwandlungsprozess Kracken ist.

31. Verfahren nach Anspruch 29, wobei der Kohlenwasserstoffumwandlungsprozess Hydrokracken ist.

32. Verfahren nach Anspruch 29, wobei der Kohlenwasserstoffumwandlungsprozess eine Hydrierung ist.

33. Verfahren nach Anspruch 29, wobei der Kohlenwasserstoffumwandlungsprozess eine Polymerisation ist.

34. Verfahren nach Anspruch 29, wobei der Kohlenwasserstoffumwandlungsprozess eine Alkylierung ist.

35. Verfahren nach Anspruch 29, wobei der Kohlenwasserstoffumwandlungsprozess eine Reformierung ist.

36. Verfahren nach Anspruch 29, wobei der Kohlenwasserstoffumwandlungsprozess eine Hydrobehandlung ist.

## O 043 562

37. Verfahren nach Anspruch 29, wobei der Kohlenwasserstoffumwandlungsprozess eine Isomerisierung ist.

38. Verfahren nach Anspruch 37, wobei die Isomerisierung die Xylo-Isomerisierung ist.

### 5 Revendications

1. Aluminophosphates cristallins ayant chacun une ossature structurale dont la composition chimique exprimée d'après les rapports molaires d'oxydes, est la suivante:

10  $\text{Al}_2\text{O}_3:1,0 \pm 0,2 \text{ P}_2\text{O}_5$ :

caractérisés en ce que chacune desdites ossatures structurales est microporeuse, les pores étant uniformes et ayant des diamètres nominaux compris dans l'intervalle de 0,3 à 1,0 nm, avec une capacité d'adsorption intracristalline pour l'eau sous pression de 6,13 mbars et à 24°C d'au moins 15 3,5% en poids, l'adsorption et la désorption de l'eau étant entièrement réversibles cependant que la même topologie essentielle d'ossature est conservée tant à l'état hydraté qu'à l'état déshydraté.

2. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 2.

3. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction de 20 rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 4.

4. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 6.

5. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 8.

25 6. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 10.

7. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 12.

8. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des 30 rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 13.

9. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 15.

10. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 17.

35 11. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 19.

12. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 21.

13. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des 40 rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 23.

14. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre correspondant essentiellement au tableau 24.

15. Aluminophosphate cristallin suivant la revendication 1, qui a un diagramme de diffraction des rayons X à l'état de poudre présentant au moins les espacements d indiqués sur le tableau 25.

45 16. Aluminophosphate cristallin suivant la revendication 1, qui présente un diagramme de diffraction des rayons X à l'état de poudre correspondant essentiellement au tableau 26.

17. Procédé de préparation d'un aluminophosphate cristallin microporeux ayant une composition chimique exprimée, d'après les rapports molaires des oxydes, par la formule

50  $\text{Al}_2\text{O}_3:1,0 \pm 0,2 \text{ P}_2\text{O}_5$ ,

caractérisé par la formation d'un mélange réactionnel dont la composition, d'après les rapports molaires des oxydes, s'exprime par

$\text{Al}_2\text{O}_3:1 \pm 0,5 \text{ P}_2\text{O}_5:7—100 \text{ H}_2\text{O}$

55 et contenant environ 0,2 à 2,0 moles d'un agent organique formant matrice, par mole de  $\text{Al}_2\text{O}_3$ , et le chauffage du dit mélange réactionnel à une température d'au moins 100°C jusqu'à ce que des cristaux dudit aluminophosphate soient produits.

18. Procédé suivant la revendication 17, dans lequel le mélange réactionnel est chauffé à une température de 100 à 300°C sous pression autogène.

60 19. Procédé suivant la revendication 18, dans lequel le mélange réactionnel a pour composition, exprimée d'après les rapports molaires d'oxydes,

$\text{Al}_2\text{O}_3:0,8—1,2 \text{ P}_2\text{O}_5:25—75 \text{ H}_2\text{O}$

65 et est chauffé à une température de 125 à 200°C.

**O 43 562**

20. Procédé suivant la revendication 19, dans lequel la source de  $P_2O_5$  est l'acide phosphorique, la source de  $Al_2O_3$  est l'oxyde d'aluminium hydraté appelé pseudoboehmite et le mélange réactionnel contient par mole de  $Al_2O_3$  0,5 à 1,5 mole d'un agent organique formant matrice, 40 à 50 moles de  $H_2O$  et environ 1,0 mole de  $P_2O_5$ .

5 21. Procédé suivant la revendication 19, dans lequel l'agent formant matrice est choisi dans le groupe comprenant l'hydroxyde de tétrapropylammonium; l'hydroxyde de tétraéthylammonium; la tripropylamine; la triéthylamine; la triéthanamine; la pipéridine; la cyclohexylamine; la 2-méthylpyridine; la N,N-diméthylbenzylamine; la N,N-diéthyléthanamine; la dicyclohexylamine; la N,N-diméthyléthanamine; la choline; la N,N-diméthylpipérazine; le 1,4-diazabicyclo(2,2,2)octane; la N-méthyldiéthanamine; la N-méthyléthanamine; la N-méthylpipéridine; la 3-méthylpipéridine; la N-méthylcyclohexylamine; la 3-méthylpyridine; la 4-méthylpyridine; la quinuclidine; et le dihydroxyde de N,N'-diméthyl-1,4-diazabicyclo(2,2,2)-octane.

10 22. Procédé suivant la revendication 19, dans lequel l'agent formant matrice est choisi dans le groupe comprenant l'hydroxyde de tétraméthylammonium; l'hydroxyde de tétraéthylammonium; l'hydroxyde de tétrabutylammonium; l'hydroxyde de térapentylammonium; la di-(n-butyl)-amine; la néopentylamine; la di-(n-pentyl)-amine; l'isopropylamine et la tertio-butylamine.

15 23. Procédé suivant la revendication 19, dans lequel l'agent formant matrice est une alkylamine dont le groupe alkyle contient 2 à 7 atomes de carbone.

20 24. Procédé suivant la revendication 19, dans lequel l'agent formant matrice est choisi entre l'éthylénediamine et la 2-imidazolidone.

25 25. Procédé suivant la revendication 23, dans lequel l'alkylamine est la di-(n-propyl)amine.

26. Procédé suivant la revendication 19, dans lequel l'agent formant matrice est un sel polymérique d'ammonium quaternaire  $[(C_{14}H_{33}N_2)(OH)_2]_x$ , où X a une valeur d'au moins 2.

27. Procédé pour séparer une espèce moléculaire polaire ayant un diamètre moléculaire efficace de moins d'environ 1,0 nm d'un mélange avec une espèce moléculaire moins polaire par mise en contact dudit mélange avec au moins un aluminophosphate suivant la revendication 1, ledit aluminophosphate étant au moins partiellement déshydraté au début de la mise en contact et ayant un diamètre de pore assez grand pour adsorber l'espèce moléculaire plus polaire.

28. Procédé suivant la revendication 27, dans lequel l'espèce moléculaire plus polaire est l'eau.

30 29. Procédé pour convertir un hydrocarbure qui consiste à faire entrer ledit hydrocarbure en contact dans des conditions de transformation d'un hydrocarbure avec un aluminophosphate suivant la revendication 1.

30 30. Procédé suivant la revendication 29, dans lequel le processus de transformation d'un hydrocarbure est un craquage.

35 31. Procédé suivant la revendication 29, dans lequel le processus de transformation d'un hydrocarbure est un hydrocraquage.

32. Procédé suivant la revendication 29, dans lequel le processus de transformation d'un hydrocarbure est une hydrogénéation.

33. Procédé suivant la revendication 29, dans lequel le processus de transformation d'un hydrocarbure est une polymérisation.

34. Procédé suivant la revendication 29, dans lequel le processus de transformation d'un hydrocarbure est une alkylation.

35. Procédé suivant la revendication 29, dans lequel le processus de transformation d'un hydrocarbure est un reformage.

45 36. Procédé suivant la revendication 29, dans lequel le processus de transformation d'un hydrocarbure est un hydrotraitement.

37. Procédé suivant la revendication 29, dans lequel le processus de transformation d'un hydrocarbure est une isomérisation.

38. Procédé suivant la revendication 37, dans lequel l'isomérisation est une isomérisation du xylène.